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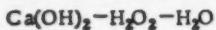
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SYSTEMS CONTAINING CONCENTRATED HYDROGEN PEROXIDE

COMMUNICATION 4. SOLUBILITY ISOTHERMS OF THE TERNARY SYSTEM



S. Z. Makarov and N. K. Grigoryeva

There are indications in the literature of the existence of the following calcium peroxy compounds: calcium peroxide octahydrate $\text{CaO}_2 \cdot 8\text{H}_2\text{O}$, calcium peroxide dihydrate $\text{CaO}_2 \cdot 2\text{H}_2\text{O}$, anhydrous calcium peroxide CaO_2 , and calcium peroxide diperhydrate, which contains hydrogen peroxide of crystallization and has the formula $\text{CaO}_2 \cdot 2\text{H}_2\text{O}_2$. Attempts have been made to demonstrate the existence of calcium tetroxide CaO_4 as an impurity in CaO_2 . However, the material in the literature on this question is very contradictory and gives rise to considerable doubt.

Calcium peroxide was prepared by Thenard [1] in 1818 in the form of $\text{CaO}_2 \cdot 8\text{H}_2\text{O}$ by the reaction of aqueous hydrogen peroxide solutions with lime water. In 1866 Schöne [2], and in 1873 Conroy [3], confirmed this formula; Schöne stated that the crystals of calcium peroxide octahydrate are square in shape. Calcium peroxide formed the subject of some careful investigations by Forcrand [4, 5, 6], who studied heats of reaction for the action of various amounts of hydrogen peroxide on calcium oxide and obtained two compounds: $\text{CaO}_2 \cdot 2\text{H}_2\text{O}$ and $\text{CaO}_2 \cdot 8\text{H}_2\text{O}$. He related the degree of hydration of the calcium peroxide to the ratio of CaO to H_2O_2 and the reaction temperature.

Riesenfeld and Nottebohm [7] showed that, apart from calcium peroxide di- and octa-hydrates, anhydrous calcium peroxide could be obtained directly from calcium salts, aqueous ammonia, and hydrogen peroxide by the use of suitable conditions of concentration and temperature; they showed also that CaO_2 exists in two modifications. These authors prepared also a diperhydrate of calcium peroxide by reaction of concentrated H_2O_2 with $\text{CaO}_2 \cdot 8\text{H}_2\text{O}$ at low temperature. Traube and Schulze [8] made a study of calcium peroxide and postulated the existence of a higher calcium peroxide CaO_4 , accompanying CaO_2 as an impurity to the extent of 5-8%, but they did not isolate CaO_4 in the pure state.

Kotov and Raikhshtein [9] and Kazarnovsky [10] studied the X-ray structures of alkali and alkaline-earth peroxides. These peroxides have lattices of the calcium carbide type, elongated in one direction owing to the elongated form of the O_2^{--} ion. The crystals, therefore, belong to the tetragonal, and not the cubical, syngony. The two oxygen atoms are equivalent, being linked by a homopolar bond.

Ehrlich [11] carried out determinations of the magnetic susceptibilities of calcium di- and tetra-oxides in a calcium peroxide sample containing about 5% of CaO_4 and established that CaO_4 contains the O_2^{--} ion.

Astakhov and Getsov [12], who also studied the structure of calcium tetroxide, concluded that CaO_4 has an ionic lattice formed by Ca^{++} and O_2^{--} ions.

It must be emphasized that all of the investigations on the peroxy compounds of calcium have been of a purely preparative nature: they cannot answer the question of the exact compositions and natures of the compounds formed, of their fields of existence, of the conditions under which the interaction products formed from hydrogen peroxide and aqueous solutions of calcium salts can be obtained, and of the chemical changes that occur in the system.

Methods of physicochemical analysis, which have been developed by N. S. Kurnakov into an independent branch of physical chemistry, can very well provide the answers to these questions. These methods of physicochemical analysis have been successfully applied to the study of the systems: 1) sodium carbonates and H_2O_2 [13], and 2) urea and H_2O_2 [14]. This method is now applied for the first time to a system in which Ca(OH)_2 and H_2O_2 are components.

The binary system $\text{Ca}(\text{OH})_2-\text{H}_2\text{O}$ has been studied by many investigators. Data published in the period 1878-1934 on the solubility of CaO in water have been collected by Seidell [15]. Recent results, obtained by Haslam [16] and Bossett [17], indicate that the solubility of $\text{Ca}(\text{OH})_2$ falls as the temperature rises. The solubility of $\text{Ca}(\text{OH})_2$ in water falls almost linearly, and the existence of any hydrates is, therefore, excluded.

From 1900 onwards, the binary system $\text{H}_2\text{O}_2-\text{H}_2\text{O}$ has been investigated by many chemists. It was at first considered that solid solutions were formed in all of the solid phases of the system. However, the work of Foley and Giguere [18], which appeared in 1951, completely refuted the existence of solid solutions of water in hydrogen peroxide and of hydrogen peroxide in water. Independently, Mironov and Bergman [19] also established the absence of solid solutions in this system.

EXPERIMENTAL

The ternary system $\text{Ca}(\text{OH})_2-\text{H}_2\text{O}_2-\text{H}_2\text{O}$ was investigated by the solubility method at three temperatures, 0° , -10° , and -21° , under isothermal conditions. The system was studied over a wide range of hydrogen peroxide concentration, the solid phases being investigated by chemical and thermal analysis. In the solutions of this system equilibrium was established by stirring for 1-2 hours, depending on the H_2O_2 content of the liquid phase. At high H_2O_2 concentrations, the establishment of equilibrium was complicated by the decomposition of the hydrogen peroxide, resulting in a corresponding displacement of the equilibrium.

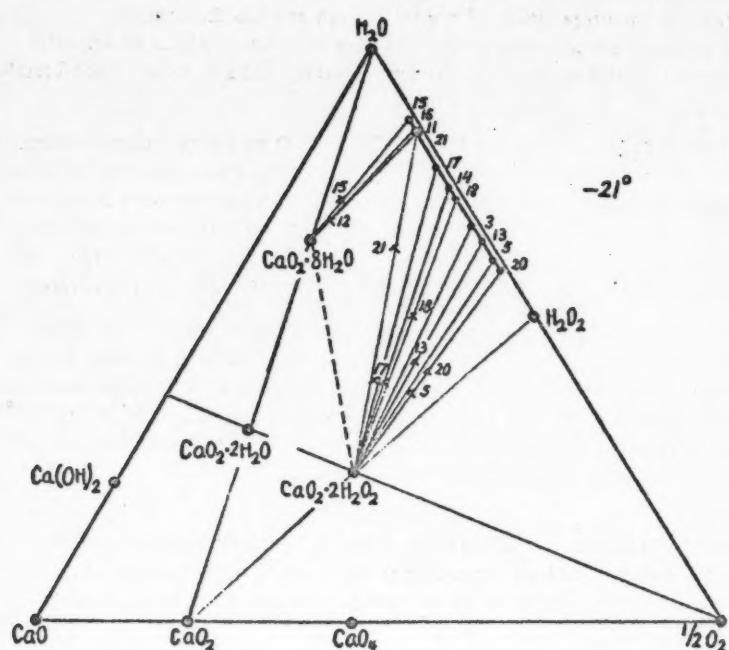


Fig. 1

Test samples for determination of active oxygen were placed in small beakers for weighing together with borate stabilizers. The samples for the determination of CaO were weighed in beakers without the addition of stabilizers. Active oxygen was determined by titration in presence of sulfuric acid with 0.1 N KMnO_4 . Calcium, after precipitation as oxalate, was also titrated with 0.1 N KMnO_4 . The analytical results were calculated as CaO , H_2O_2 , and H_2O . The results (% by weight) were plotted on the triangular diagram $\text{CaO}-\text{H}_2\text{O}_2-\text{H}_2\text{O}$. The compositions of the solid phases were determined graphically and analytically by the residue method.

Study of the -21° isotherm of this system is confined to H_2O_2 concentrations in the range 26-82%, since, according to Foley and Giguere and also to Mironov and Bergman, hydrogen peroxide solutions containing less than 26% or more than 82% of H_2O_2 are already frozen at -21° . For the -10° isotherm the non-freezing region is extended to 15-91% H_2O_2 .

Substances of high purity were used: $\text{Ca}(\text{OH})_2$ containing 76.02% of CaO and 23.98% of H_2O , but no detectable traces of CO_2 , and prepared from calcium hydroxide (Glavkhimreaktiv "pure" brand) by calcination at 800-900° followed by slaking with water to $\text{Ca}(\text{OH})_2$ with exclusion of carbon dioxide; calcium peroxide octahydrate, containing 7.4% of active oxygen and 26.77% of CaO , and prepared by the ammonia method from $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$; calcium peroxide containing 20.5% active oxygen; hydrogen peroxide of various concentrations, freed from stabilizer by fractional vacuum distillation.

Test samples of the liquid phases and residues were taken by filtration of the mixture through a Schott No. 2 or No. 3 funnel (under suction), the operation being carried out isothermally at the temperature of the experiment. Both the liquid phase and the residue were analyzed for active oxygen and calcium.

TABLE 1

-21° Isotherm for the System $\text{Ca}(\text{OH})_2$ – H_2O_2 – H_2O

Point No.	Concn. of orig. H_2O_2 (% by wt.)		Composition of liquid phase (% by weight)			Composition of residue (% by weight)			Composition of solid phases	Starting material
	as	as active	$\frac{1}{2}\text{O}_2$	CaO	H_2O	$\frac{1}{2}\text{O}_2$	CaO	H_2O		
	H_2O_2	O_2								
12	24.5	11.5	11.5	0.81	87.6	9.1	21.7	69.2	$\text{CaO}_2 \cdot 8\text{H}_2\text{O}$	$\text{Ca}(\text{OH})_2$
16	26.0	12.2	11.8	0.83	87.4	9.0	16.5	74.5	The same	$\text{CaO}_2 \cdot 8\text{H}_2\text{O}$
11	28.0	13.2	13.0	0.82	86.0	10.0	17.0	73.0	"	$\text{Ca}(\text{OH})_2$
15	30.0	14.1	12.7	0.90	86.4	9.6	17.5	72.9	"	$\text{CaO}_2 \cdot 8\text{H}_2\text{O}$
21	32.6	15.3	14.1	0.13	85.8	20.9	14.7	64.7	$\text{CaO}_2 \cdot 2\text{H}_2\text{O}_2$	$\text{CaO}_2 \cdot 8\text{H}_2\text{O}$
8	44.0	20.7	16.9	0.38	82.7	28.7	32.2	39.1	The same	$\text{Ca}(\text{OH})_2$
17	50.0	23.5	19.7	0.40	79.9	30.3	28.6	41.1	"	$\text{CaO}_2 \cdot 8\text{H}_2\text{O}$
2	52.0	24.5	21.2	0.38	78.4	28.9	25.4	45.7	"	$\text{Ca}(\text{OH})_2$
6	60.0	28.2	25.6	0.37	74.0	30.5	28.7	40.8	"	$\text{Ca}(\text{OH})_2$
14	60.5	28.4	23.2	0.37	76.4	32.8	29.0	38.2	"	$\text{CaO}_2 \cdot 8\text{H}_2\text{O}$
18	60.0	28.2	25.0	0.55	74.4	29.7	18.0	52.3	"	$\text{CaO}_2 \cdot 8\text{H}_2\text{O}$
3	70.0	32.9	30.2	0.33	69.5	32.0	31.9	36.1	"	$\text{Ca}(\text{OH})_2$
10	79.0	37.1	34.5	0.28	65.3	33.2	23.4	44.4	"	$\text{Ca}(\text{OH})_2$
13	83.0	39.0	33.1	0.33	66.6	33.1	22.0	44.9	"	$\text{Ca}(\text{OH})_2$
7	83.6	39.3	36.2	0.21	63.6	34.4	20.2	45.4	"	$\text{Ca}(\text{OH})_2$
5	88.0	41.3	35.7	0.18	64.1	34.8	26.0	39.2	"	$\text{Ca}(\text{OH})_2$
20	95.6	44.9	38.0	0.23	61.8	35.0	20.8	44.2	"	$\text{CaO}_2 \cdot 8\text{H}_2\text{O}$

TABLE 2

-10° Isotherm for the System $\text{Ca}(\text{OH})_2$ – H_2O_2 – H_2O

Point No.	Concn. of orig. H_2O_2 (% by wt.)		Composition of liquid phase (% by weight)			Composition of residue (% by weight)			Composition of solid phases	Starting material
	as	as active	$\frac{1}{2}\text{O}_2$	CaO	H_2O	$\frac{1}{2}\text{O}_2$	CaO	H_2O		
	H_2O_2	O_2								
17	18.0	8.8	7.0	0.25	92.7	7.7	21.7	71.7	$\text{CaO}_2 \cdot 8\text{H}_2\text{O}$	$\text{Ca}(\text{OH})_2$
15	25.4	11.9	10.3	0.50	89.2	9.5	17.8	72.6	$\text{CaO}_2 \cdot 8\text{H}_2\text{O}$	The same
23	27.5	12.9	9.9	0.48	89.6	17.4	21.6	61.0	transition points $\text{CaO}_2 \cdot 8\text{H}_2\text{O} + \text{CaO}_2 \cdot 2\text{H}_2\text{O}_2$	"
24	27.5	12.9	10.5	0.56	88.9	14.7	18.5	66.8		"
25	27.5	12.9	9.2	0.40	90.4	18.5	19.9	61.6	$\text{CaO}_2 \cdot 2\text{H}_2\text{O}_2$	"
2	30.4	14.3	10.0	0.32	89.7	20.3	18.6	61.2	$\text{CaO}_2 \cdot 2\text{H}_2\text{O}_2$	"
22	39.0	18.3	14.4	0.36	85.2	26.0	23.0	51.0	The same	"
4	46.0	21.6	17.7	0.36	82.0	25.6	22.6	51.8	"	"
26	56.0	26.3	21.2	0.35	78.5	30.5	29.5	40.0	"	"
21	58.0	27.3	24.6	0.36	75.0	30.0	26.3	43.7	"	$\text{CaO}_2 \cdot 8\text{H}_2\text{O}$
5	61.3	28.8	24.3	0.33	75.3	29.4	29.6	41.0	"	$\text{Ca}(\text{OH})_2$
8	61.3	28.8	27.0	0.36	72.7	29.6	29.5	40.9	"	CaO_2
20	64.0	30.1	27.2	0.32	72.5	30.6	25.6	43.8	"	$\text{Ca}(\text{OH})_2$
19	68.5	32.6	29.2	0.30	70.5	30.9	26.1	42.9	"	The same
16	75.0	35.0	32.5	0.25	67.2	32.8	21.3	45.9	"	"
27	83.0	39.0	35.8	0.23	64.0	34.0	23.5	42.5	"	$\text{CaO}_2 \cdot 8\text{H}_2\text{O}$
6	84.0	39.5	36.3	0.21	63.5	35.2	16.3	48.6	"	$\text{Ca}(\text{OH})_2$
9	91.0	42.8	40.6	0.16	59.2	35.7	25.4	39.3	"	CaO_2
28	97.0	45.6	43.5	0.10	56.4	39.0	19.5	41.5	"	$\text{CaO}_2 \cdot 8\text{H}_2\text{O}$
14	97.5	45.8	43.3	0.07	56.6	40.1	17.6	42.3	"	$\text{Ca}(\text{OH})_2$

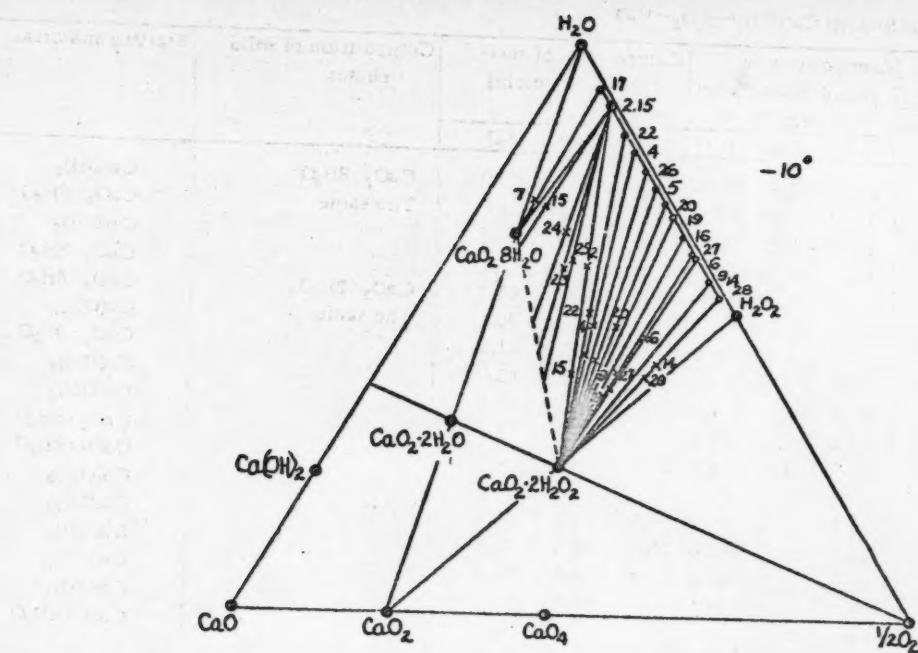


Fig. 2

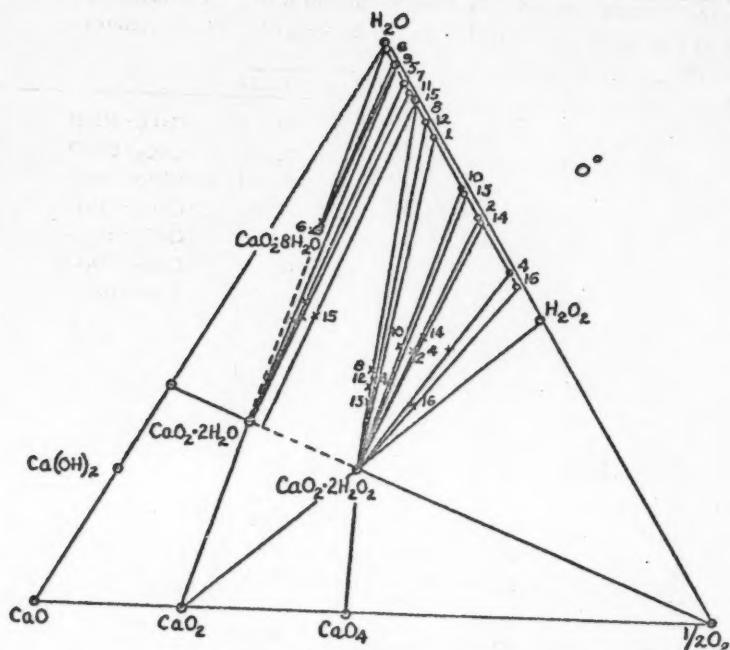


Fig. 3

TABLE 3

0° Isotherm for the System $\text{Ca}(\text{OH})_2 - \text{H}_2\text{O}_2 - \text{H}_2\text{O}$

Point No.	Concn. of orig. H_2O_2 (% by wt.)		Composition of liquid phase (% by weight)			Composition of residue (% by weight)			Composition of solid phases	Starting material		
	as		as active									
	H_2O_2	O_2	$\frac{1}{2}\text{O}_2$	CaO	H_2O	$\frac{1}{2}\text{O}_2$	CaO	H_2O				
6	3.8	1.8	None	0.05	99.95	6.2	27.9	65.8	$\text{CaO}_2 \cdot 8\text{H}_2\text{O}$	$\text{Ca}(\text{OH})_2$		
9	12.1	5.8	2.25	0.40	97.35	7.8	25.4	66.8	$\text{CaO}_2 \cdot 8\text{H}_2\text{O}$	The same		
5	12.8	6.0	3.40	0.10	96.50	11.5	34.6	53.8	$\text{CaO}_2 \cdot 2\text{H}_2\text{O}$	"		
7	22.5	10.6	6.60	0.22	93.18	13.8	36.4	49.8	The same	"		
11	26.0	12.2	8.05	0.26	91.69	14.1	35.1	50.9	"	"		
15	28.0	13.2	9.60	0.32	90.1	14.5	33.3	52.2	"	"		
12	31.0	14.6	13.2	0.61	86.19	28.0	30.5	41.5	$\text{CaO}_2 \cdot 2\text{H}_2\text{O}_2$	$\text{CaO}_2 \cdot 8\text{H}_2\text{O}$		
8	31.4	14.8	9.3	0.33	90.37	26.7	30.5	42.8	The same	$\text{Ca}(\text{OH})_2$		
1	44.0	20.7	15.6	0.37	84.03	26.8	27.2	46.0	"	The same		
10	60.0	28.2	24.5	0.37	75.13	28.8	23.7	47.5	"	"		
13	60.0	28.2	24.9	0.37	74.73	31.2	33.5	35.3	"	$\text{CaO}_2 \cdot 8\text{H}_2\text{O}$		
2	70.0	32.9	29.7	0.30	70.0	31.6	21.9	46.5	"	$\text{Ca}(\text{OH})_2$		
4	88.0	41.3	39.1	0.14	60.76	35.6	18.6	45.8	"	$\text{Ca}(\text{OH})_2$		
14	96.7	45.4	30.4	0.27	69.33	32.2	19.0	48.8	"	$\text{CaO}_2 \cdot 8\text{H}_2\text{O}$		
16	97.0	45.6	41.4	0.14	58.56	36.5	26.3	37.2	"	$\text{CaO}_2 \cdot 8\text{H}_2\text{O}$		

The results of the investigation of the ternary system $\text{Ca}(\text{OH})_2 - \text{H}_2\text{O}_2 - \text{H}_2\text{O}$ at the three temperatures -21° , -10° , and 0° are given in Tables 1, 2, and 3, and are represented graphically in Figs. 1, 2, and 3. They show successive changes in the compositions of the liquid and equilibrium solid phases as the hydrogen peroxide content of the solutions increases.

The solubility isotherms of the system $\text{Ca}(\text{OH})_2 - \text{H}_2\text{O}_2 - \text{H}_2\text{O}$ at -21° and -10° are characterized by two solid phases of composition $\text{CaO}_2 \cdot 8\text{H}_2\text{O}$ and $\text{CaO}_2 \cdot 2\text{H}_2\text{O}_2$. At -21° the field of existence of calcium peroxide octahydrate is very limited, namely, 24.5-28% H_2O_2 in the liquid phase; at -10° it is 14.8-21.9% H_2O_2 . A very small increase in the H_2O_2 concentration of the liquid phase results in the immediate formation of calcium peroxide diperhydrate, the addition product formed by H_2O_2 with anhydrous CaO_2 . The upper limit of the field of existence of $\text{CaO}_2 \cdot 2\text{H}_2\text{O}_2$ is determined by the temperature at which hydrogen peroxide solutions freeze, namely: at -21° the H_2O_2 concentration reaches 81%, and at -10° it reaches 92%.

The 0° solubility isotherm is characterized by the presence of three solid phases of composition:

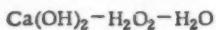
$\text{CaO}_2 \cdot 8\text{H}_2\text{O}$, existing up to 5-6% H_2O_2 in the liquid phase;
 $\text{CaO}_2 \cdot 2\text{H}_2\text{O}$, existing in the range 7-20% H_2O_2 ;
 $\text{CaO}_2 \cdot 2\text{H}_2\text{O}_2$, existing from 20 to 88% H_2O_2 .

When the H_2O_2 content of the liquid phase is above 88% it is very difficult to establish equilibrium in the system owing to vigorous decomposition of hydrogen peroxide and products of its reaction with the solid phases taken.

Calcium peroxide dihydrate $\text{CaO}_2 \cdot 2\text{H}_2\text{O}$ made its first appearance in the study of the 0° isotherm. At lower temperatures no field of existence was observed.

SUMMARY

1. A study of the interaction of aqueous solutions of calcium hydroxide with hydrogen peroxide over a wide range of concentrations, carried out by the solubility method applied to the ternary system



at 0° , -10° , and -21° , has made it possible to determine the actual composition and limits of existence of the stable solid phases.

2. The calcium peroxy compounds whose existence is fully established by the study of the ternary system $\text{Ca}(\text{OH})_2 - \text{H}_2\text{O}_2 - \text{H}_2\text{O}$ at 0° , -10° , and -21° are: $\text{CaO}_2 \cdot 8\text{H}_2\text{O}$; $\text{CaO}_2 \cdot 2\text{H}_2\text{O}$ and $\text{CaO}_2 \cdot 2\text{H}_2\text{O}_2$.

3. Formation of calcium peroxide octahydrate occurs under restricted conditions at low hydrogen peroxide concentrations.

4. Calcium peroxide diperhydrate is formed over a wide range of hydrogen peroxide concentrations and is relatively stable only at low temperatures.

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Peroxy Compound Laboratory of the USSR
Academy of Sciences

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SOLUBILITY OF THE ELEMENTS IN TITANIUM

I. I. Kornilov

Titanium, an element of Group IV of Mendeleev's periodic system of the elements, is generally regarded as a rare element, although in comparison with some other "common" elements it is widely distributed in the earth's crust [1, 2, 3]. Among metals of practical importance, it occupies fourth place with respect to its abundance in the earth's crust: of the 15% total metal content, aluminum accounts for 8.14%, iron 5.12%, magnesium 2.10%, and titanium 0.61%. The content of all of the remaining metals, including such "common" metals as nickel, chromium, copper, and others, is only 0.2%.

Methods have now been developed for the preparation of metallic titanium [1, 2, 3, 4]. It is obtained by the reduction of titanic chloride with molten magnesium by the reaction: $TiCl_4 + 2Mg \rightarrow Ti + 2MgCl_2$; and also by the thermal dissociation of titanic iodide according to the reaction: $TiI_4 \rightarrow Ti + 2I_2$, and condensation of the metallic titanium on an incandescent molybdenum wire [4, 5]. The second method gives the purest titanium: the so-called "iodide" titanium. Table 1 gives the chemical compositions of titanums obtained by the two methods.

The principal properties of the titanums obtained from $TiCl_4$ and from TiI_4 are given in Table 2 [2, 3].

TABLE 1

Chemical Composition of Metallic Titanium

Method of preparation	Ti%	Fe%	Al%	Si%	Mg%
From titanic chloride	99.1	0.06-0.09	—	0.005-0.01	0.03-0.05
From titanic iodide	99.9	0.01-0.05	0.05-0.1	0.01-0.05	0.005
Method of preparation	Mo%	Ca%	C%	N%	O%
From titanic chloride	—	—	0.01-0.04	0.006-0.03	—
From titanic iodide	0.05-0.1	0.01-0.05	0.02-0.03	0.002-0.009	—
					0.09-0.20

TABLE 2

Properties of Titanium Prepared by Different Methods

Property	from $TiCl_4$	from TiI_4
Melting point (°C)	1725	1725
Type of crystal-lattice		
α -modification		Hexagonal
β -modification		Body-centered
Temperature of polymorphous transition (°C)	882	885
Specific gravity (g/cc)	4.5	4.5
Resistivity ($\times 10^{-4}$ ohm.cm)	0.475	0.475
Coefficient of linear expansion at 20°		$8.5 \cdot 10^{-6}$
Breaking strength (kg/sq.mm)	49-56	27-34
Extension at break (%)	25-30	40
Brinell hardness (kg/sq.mm)	220	100-160

The properties of titanium, like those of other metals, are greatly affected by alloying with other metals, or, in certain cases, metalloids. Titanium is able to form solid solutions and compounds having bonds of a metallic character with many metals. The general laws for the formation of metallic solid solutions and compounds [6, 7], which have been derived by application of Mendeleev's periodic law of the elements, are equally applicable to a study of the interaction of titanium with other elements of the periodic system.

TABLE 3

Dependence of the Solubility of the Elements in Titanium on the Difference in Atomic Diameters (arranged by Groups)

Group	Element	Atomic diameter	Difference (%)	Solubility according to literature (with reference), or expected solubility	
				(no reference)	
1	2	3	4	5	
<u>Subgroup A</u>					
1	H	1.20	-	Solid interstitial solutions and titanium hydride TiH_2 [10]	
1	Li	3.13	6.8		
1	Na	3.83	30.7	Insoluble	
1	K	4.76	62.4	"	
1	Rb	5.40	84.3	"	
1	Cs	5.40	84.3	"	
2	Be	2.25	23.2	Very limited solubility [2]	
2	Mg	3.20	9.5	Insoluble	
2	Ca	3.93	34.1	"	
2	Sr	4.29	46	"	
2	Ba	4.48	52.9	"	
2	Ra	-	-	"	
3	B	1.94	34.3	Very limited solid solutions [11]	
3	Al	2.80	4.4	Large field of solid solutions [12]. Break in solubility due to difference in crystal lattice	
3	Sc	3.02	3.0	Continuous solubility	
3	Y	3.62	23.5	Very limited solubility	
3	Ti	2.93	-	Continuous solubility	
4	Zr	3.19	8.8	Continuous solubility of the two modifications α and β [14]	
4	Hf	3.17	8.2	Continuous solubility of the two modifications α and β	
4	Th	3.60	23.2	Very limited solubility	
5	V	2.69	8.2	Continuous solubility in β -Ti [16]	
5	Nb	2.94	0.4	The same in β -Ti [17]	
5	Ta	2.94	0.4	" in β -Ti [18]	
6	Cr	2.57	12.3	" in β -Ti [19]	
6	Mo	2.80	4.4	" in β -Ti [20]	
6	W	2.82	4.0	Considerable field of solid solutions in β -Ti [18]	
6	U	2.81	4.1	Break in solubility due to difference in crystal lattice	
7	Mn	2.60	11.25	Limited solubility in α - and β -Ti [21]	
7	Re	2.75	6.1	Continuous solubility in α -Ti	
8	Fe	2.54	13.3	Limited solubility in α - and β -Ti [22]	
8	Co	2.50	14.7	Limited solubility in α - and β -Ti [23]	
8	Ni	2.49	15.0	Limited solubility in α - and β -Ti [24]	
8	Ru	2.67	8.9	The same	
8	Rh	2.68	8.5	"	
8	Pd	2.75	6.1	Break in solubility due to difference in crystal lattice	
8	Os	2.70	7.9	The same	
8	Ir	2.71	7.1	"	
8	Pt	2.88	1.6	"	
<u>Subgroup B</u>					
1	Cu	2.55	12.9	Limited solubility in α - and β -Ti [25]	
1	Ag	2.883	1.6	Limited solubility in α - and β -Ti [25]	
1	Au	2.877	1.81	Limited solubility in α - and β -Ti	
2	Zn	2.748	6.2		
2	Cd	3.042	3.82	Insoluble	
2	Hg	3.10	5.8		
3	Ga	2.74	6.5		
3	In	3.138	17.1	Insoluble	
3	Tl	3.427	16.9		
4	C	1.54	47.5	Very limited solubility in α - and β -Ti [27, 28]	

TABLE 3 (continued)

1	2	3	4	5
4	Si	2.34	20.1	Limited solubility in α - and β -Ti [29]
4	Ge	2.78	5.1	Limited solubility in α - and β -Ti
4	Sn	3.168	8.15	Limited solubility in α - and β -Ti [30]
4	Pb	3.494	19.2	Insoluble [30]
5	N	1.42	51.5	Very limited solubility in α - and β -Ti [32, 33]
5	P	2.20	25.0	Very limited solubility in α - and β -Ti
5	As	2.80	4.45	Limited solubility in α - and β -Ti
5	Sb	3.228	10.2	Limited solubility in α - and β -Ti [30]
5	Bi	3.640	24.2	Insoluble
6	O	1.32	55.0	Limited solubility in α - and β -Ti [36, 37, 38]

As already shown in the case of the solubility of elements in iron, nickel, and chromium [8, 9], the following conditions are favorable for the formation of solid solutions in these metals:

1. similarity in the chemical properties of the metals, which is determined by their positions in the periodic system;
2. a small difference in interatomic distances, not exceeding 8-10% for the formation of continuous solid solutions and 14-16% for the formation of limited solid solutions;
3. isomorphism of crystal structure (for the formation of continuous solid solutions).

When these conditions are observed, the tendency for metals to form solid solutions with one another is at its greatest. These same conditions are applicable to the examination of the question of the solubility of the elements in titanium.

Let us examine the solubility of the elements in titanium according to the groups of Mendeleev's system.

Table 3 includes the elements of the A and B subgroups, listed separately, the elements that interact with titanium to form only compounds of an ionic nature, (halogens, sulfur and its analogs, etc.) and do not form solid solutions or compounds having a bond of metallic character not being included.

1. Solubility in Titanium of Elements of the A Subgroups

Among elements of Group I, only hydrogen at low concentrations forms limited solid solutions of the interstitial type. At high hydrogen concentrations, a titanium hydride of the type TiH_2 is formed in titanium [10]. Apart from lithium, the remaining Group I metals, the alkali metals, differ too much from titanium in atomic diameter, and, therefore, should not form solid solutions with it.

Lithium does not differ greatly in atomic diameter (6.8%). At high temperatures, owing to the great difference between titanium and lithium in coefficient of expansion, this difference will increase to such an extent that it will become unfavorable to the replacement of titanium in the crystal lattice by lithium. These circumstances will prevent the formation of an extensive field of solid solutions of lithium in titanium.

Group II metals, apart from magnesium, have atomic diameters that bear unfavorable ratios to the atomic diameter of titanium. With the exception of beryllium, they should not form solid solutions with titanium. The behavior of magnesium is analogous to that of lithium. As experiment shows, magnesium does not react with titanium and does not form solid solutions with it. For this reason, magnesium is used in the technical preparation of titanium from its compounds [1, 2, 3]; the residual magnesium impurity in the titanium is readily driven off by heat in a high vacuum, since it is present in a form that is not chemically bound to the titanium.

With regard to elements of Group III, it must be pointed out that boron, which has a small atomic diameter, can yield very dilute solid solutions. According to the literature [11], its solubility in the α - and β -modifications of titanium does not exceed 0.4%. When the boron content is high, titanium boride TiB is formed.

With aluminum, which is close to titanium in the table and does not differ greatly in atomic diameter, titanium forms solid solutions of considerable concentration. According to the literature [12], the solubility of aluminum in the β -modification of titanium is 34.5%, and in the α -modification 24.5%. Also, transformation of the β solid solution to the α solution occurs by a peritectoid reaction.

There is no information concerning the solubilities of scandium and yttrium in titanium. It may be supposed that scandium will give continuous solid solutions, since it has an isomorphous hexagonal lattice, and that very limited solid solutions will be formed with yttrium.

The Group IV elements zirconium and hafnium are analogs of titanium. All three metals have two modifications α and β , and they have isomorphous structures and close atomic diameters. All these circumstances favor the formation of continuous solid solutions in these systems; they will be continuous for both modifications. It will be clear, therefore, that the systems $Ti\beta-Zr\beta$, $Ti\beta-Hf\beta$, $Zr\beta-Hf\beta$ (with body-centered lattice) and $Ti\alpha-Zr\alpha$, $Ti\alpha-Hf\alpha$, $Zr\alpha-Hf\alpha$ (with hexagonal lattice) will have phase diagrams corresponding to the continuous solid solutions formed by the two modifications of these metals.

This type of phase diagram can be represented for titanium in the form shown in Fig. 1. In a previous paper [13] we advanced a hypothesis that has found confirmation in subsequent papers concerning the systems titanium-zirconium [14] and zirconium-hafnium [15]. Both of these systems, in both modifications, form continuous solid solutions. There are no data concerning the solubility of thorium in titanium. From the difference (23.2%) in atomic diameter, it may be supposed that the solubility in titanium will be very limited.

The Group V elements vanadium, niobium, and tantalum, which are close to titanium in the table, are close in atomic diameter and are isomorphous with the β -modification of titanium; they should give continuous solid solutions with this modification. The data in the literature are in accord with this supposition: in the systems titanium-vanadium [16], titanium-niobium [17], and titanium-tantalum [18], continuous solid solutions are in fact formed with the β -modification of titanium. These elements lower the temperature of the $\beta \rightleftharpoons \alpha$ polymorphous change of titanium to room temperature. The phase diagram for these titanium systems is similar to that for the system Fe-Ni and is given in Fig. 2.

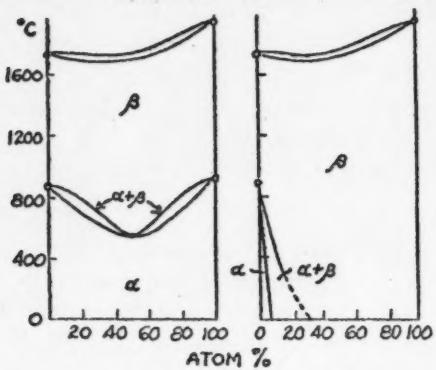


Fig. 1. Phase diagram of the system $Ti-Cr$. Fig. 2. Phase diagram of the system $Ti-V$.

The group of analogs, chromium, molybdenum, and tungsten (Group VI elements), also have favorable atomic diameters and structures isomorphous with the β -modification of titanium. All three metals may give solid solutions with β -titanium. Chromium, which is less favorable with respect to atomic diameter, forms continuous solid solutions with β -Ti and very limited solid solutions showing a eutectoid transformation with α -Ti [19].

The data in the literature on the system titanium-molybdenum [20] show that molybdenum lowers the temperature of the $\alpha \rightleftharpoons \beta$ polymorphous transformation of titanium to room temperature and gives a phase diagram similar to that of Fig. 2. According to the literature [18], the solubility of tungsten in β -Ti is about 50% by weight; its solubility in α -Ti is negligible. In the titanium-tungsten system eutectoid transformation occurs at 715° . Solid solutions should be formed also between titanium and uranium, but there are no data in the literature on this system.

Of elements of Group VII, there is information in the literature only for manganese [21]. Manganese has an appreciable solubility in the β -modification of titanium and negligible solubility in α -Ti. There is no information in the literature concerning the solubility of rhenium in titanium; the favorable relation between the atomic diameters of these two metals and the isomorphism of the structures of rhenium and α -Ti will encourage the formation of solid solutions in this system.

Elements of Group VIII, iron and its analogs, are related less favorable to titanium with respect to atomic diameter than the metals of Groups IV, V, and VI (Table 3). This explains the fact that iron and its analogs (nickel and cobalt) form only limited solid solutions with titanium, both in the β - and also in the α -modification. The solubilities of these three metals are higher in β -Ti than in α -Ti. The transformation $\beta \rightleftharpoons \alpha$ in the systems $Ti-Fe$ [22], $Ti-Ni$ [23], and $Ti-Co$ [24] has a eutectoid character and in this respect are reminiscent of the system $Fe-C$. Fig. 3 shows a typical phase diagram for such titanium systems having a eutectoid transformation.

As regards the remaining elements of Group VIII, palladium, platinum, and their analogs, there is no information in the literature about their solubilities in titanium. According to the relation of their atomic diameters to that of titanium (Table 3) they should have appreciable solubilities in titanium. Continuity of solid solutions in these systems will be absent owing to the difference between the crystal structure of titanium and those of metals of the palladium and platinum groups.

2. Solubility in Titanium of Elements of the B Subgroups

Passing to an examination of the solubility of elements of the B subgroups in titanium, we must point out that, as in the case of the solubility of elements of the B subgroups in iron, nickel, and chromium (elements of the A subgroups [7, 8, 9]) the solubility of these elements in titanium is not completely determined by the conditions given above for the formation of solid solutions of metals. They are not sufficient in all cases to explain the formation, or lack of formation, of solid solutions with titanium. It is probable that significance must be attached here to the difference in electronic structure between the atoms of the elements of these subgroups and titanium atoms and to the different nature of the interaction between valency electrons in such systems. Hence, the most characteristic feature of the interaction of titanium with these elements is the formation of metallic compounds, and not of solid solutions in appreciable concentration.

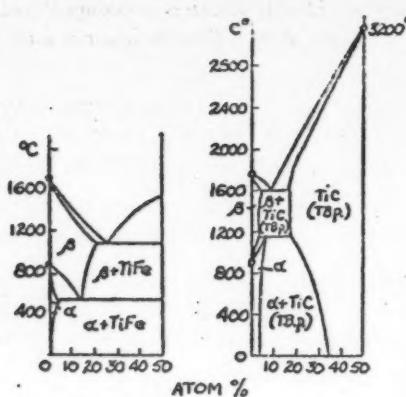


Fig. 3. Phase diagram of the system Ti-Fe. Fig. 4. Phase diagram of the system Ti-C.

It is probable that even in these cases elements of a given Group will preserve their analogous characters in their interactions with titanium. For example, the information available in the literature shows [25] that titanium forms limited solid solutions with copper that show eutectoid transformation and give a phase diagram reminiscent of that given in Fig. 3.

In the system titanium-copper the compounds Ti_2Cu , $TiCu$, Ti_2Cu_3 , and $TiCu_3$ are formed. There is no information in the literature about the interaction of titanium with the copper analogs silver and gold. It may be supposed that they will behave similarly to copper and also give limited solid solutions and form compounds with titanium.

As regards the Group II metals zinc, cadmium, and mercury, these, being low-melting metals of low boiling point, will not give solid solutions at appreciable concentrations with titanium, even when the atomic diameters are favorable. The same can be said about the following group (Group III) of low-melting metals: gallium, indium, and thalium. They also will probably not give appreciable ranges of solid solutions with titanium.

Among the elements of Group IV, carbon is of low atomic diameter. This will permit the formation of limited solid solutions of the interstitial type, and also of metallic compounds.

According to the information in the literature [26, 27, 28], carbon forms very limited solid solutions with the α - and β -modifications of titanium, and also a titanium carbide (TiC) of variable composition. The solubility of carbon in β -Ti is less than 0.25% by weight, and in α -Ti it apparently becomes less than 0.1% by weight.

The transformation of these modifications in the titanium-carbon system is effected by peritectoid reaction. The phase diagram of the Ti-C system has the form shown in Fig. 4 [28]. This shows the peritectic transformation and the variable composition of the titanium carbide compound of melting point 3200°. The type of phase diagram shown in Fig. 4 is found also in the system titanium-nitrogen.

The system titanium-silicon [29] is characterized by the formation of limited solid solutions with β - and α -titanium and by eutectic transformation. The solubility of silicon in β -Ti at the eutectic temperature is 3%, and in α -Ti, 0.3%. In this system, the compounds Ti_5Si_3 , $TiSi$, and $TiSi_2$ have been established. The phase diagram of this system is reminiscent of Fig. 3.

There are no data in the literature about the interaction of titanium with the silicon analog germanium. There is some information about the systems titanium-tin and titanium-lead [30, 31, 32]; these metals form solid solutions of low concentration with titanium [30].

Concerning the Group V element nitrogen, there are indications [27, 33, 34] of its limited solubility in α - and β -titanium (about 0.75%), the peritectoid character of the transformations, and the formation of the difficultly soluble compound titanium nitride (TiN). The phase diagram of this system will be similar to that given in Fig. 4. There is no information in the literature about the interaction of titanium with phosphorus, arsenic, and bismuth. It is possible that these elements are able to form metallic compounds with titanium, without an appreciable range of solid solutions. The available information on the system titanium-antimony does not give direct answers concerning the formation of solid solutions of antimony in titanium.

The solubility of oxygen in titanium is also very limited (not more than 0.75% by weight) [36, 37, 38]. The phase diagram of this system near to the titanium axis is similar to the diagram in Fig. 4.

As regards the interaction of titanium with sulfur and its analogs, and with the halogens: as stated above, solid solutions probably do not occur in these systems, only compounds of an ionic nature being formed.

SUMMARY

1. The solubility of the elements in titanium follows a pattern similar to that characterizing the solubility of the elements in other metals, such as iron, nickel, and chromium.

2. The formation, or non-formation, of solid solutions in binary titanium systems is associated with the relative similarity, or dissimilarity, in the properties of the elements, as indicated by Mendeleev's periodic system.

3. Metals which are titanium analogs (zirconium and hafnium), or are closely situated in Groups V and VI, and which differ little in atomic diameter and have isomorphous structures, are able to form continuous solid solutions with titanium.

4. The metals that are the most removed from titanium -elements of Groups I and II, and of Group VIII- have a lower tendency to form solid solutions. Most of the Group I and II metals do not interact with titanium in the liquid or solid state, and do not form solid solutions. Group VIII metals form only limited solid solutions.

5. Elements of low atomic diameter (H, C, N, O) are able to form solid solutions of the interstitial type in low concentration, and to form also interstitial compounds: hydrides, carbides, nitrides, and oxides of titanium.

6. The regularities established for the solubilities of the elements in titanium can be applied to the examination of the solubilities of the elements in the titanium analogs zirconium and hafnium. This will facilitate the general consideration of the phase diagrams of zirconium and hafnium systems, the great majority of which have not been studied.

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HETEROGENEOUS EQUILIBRIA IN SYSTEMS CONTAINING LITHIUM CHLORIDE AND
CHLORIDES OF GROUP II METALS

V. P. Blidin

It is known that lithium chloride interacts with many chlorides of bivalent metals, forming hydrated double salts of various types. Voskresenskaya and Yanatyeva [1], in a study of the system $\text{LiCl}-\text{MgCl}_2-\text{H}_2\text{O}$ obtained a salt of composition $\text{LiCl} \cdot \text{MgCl}_2 \cdot 7\text{H}_2\text{O}$. Basset and Sanderson [2], in a study of the system $\text{SiCl}-\text{CoCl}_2-\text{H}_2\text{O}$ found various double salts, $\text{LiCl} \cdot \text{CoCl}_2 \cdot 2\text{H}_2\text{O}$, $7\text{LiCl} \cdot 2\text{CoCl}_2 \cdot 18\text{H}_2\text{O}$, $3\text{LiCl} \cdot 2\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, and over a certain concentration range they found solid solutions. Benraht's [3] investigations established that double LiCl salts of a similar type are formed with nickel and manganese chlorides. On the other hand, in an investigation of the system $\text{LiCl}-\text{BeCl}_2-\text{H}_2\text{O}$ Novoselova and Sosnovskaya [4] established that no hydrated double salts were found in this system.

EXPERIMENTAL

As starting materials, salts having the "chemically pure" label were taken and recrystallized twice. Chlorine, according to the acidity of the medium, was determined either gravimetrically, or by Mohr titration with AgNO_3 solution. Beryllium was precipitated as hydroxide with dilute ammonia solution, and the hydroxide was dried off in a platinum crucible over a bunsen within the range 1000-1100°. Calcium was precipitated as CaC_2O_4 , converted into CaCl_2 , and determined by titration of the last compound with AgNO_3 . Barium and strontium were determined gravimetrically. Zinc and cadmium were determined "trilonometrically" with the aid of Trilon B [5]. Mercury was determined volumetrically by the method described by Korenman [6]. In all cases lithium was determined by difference from the total amount of chlorides. The solubilities in the systems were studied in an electrically heated water thermostat, the temperature being maintained constant within $\pm 0.1^\circ$ and controlled with a toluene thermoregulator. The solubilities of the salts were determined in a reaction vessel having a petroleum jelly seal. The solution in the vessel was stirred at constant temperature until equilibrium between the liquid and solid phases was attained, which required from ten hours to three days. The compositions of the solid phases were established by the Schreinemakers "residue" method. In the graphical representation of the equilibria on diagrams we expressed concentrations in percent by weight. The cosolubilities of the components were studied isothermally at 25° and 40°, with the exception of the system $\text{LiCl}-\text{HgCl}_2-\text{H}_2\text{O}$, which was studied at 30°.

The 25° and 40° isotherms of the system $\text{LiCl}-\text{BeCl}_2-\text{H}_2\text{O}$ (Table 1, Fig. 1). In the investigation of this system, it was found that when BeCl_2 was added, the viscosity of the solution increased and settling in the liquid phase lasted a long time. With increase in the LiCl concentration the viscosity diminished, and settling in the liquid phase then occupied only a short period of time.

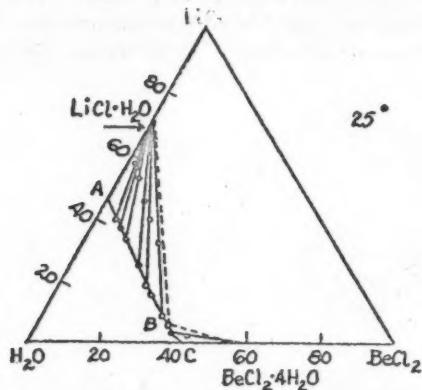


Fig. 1

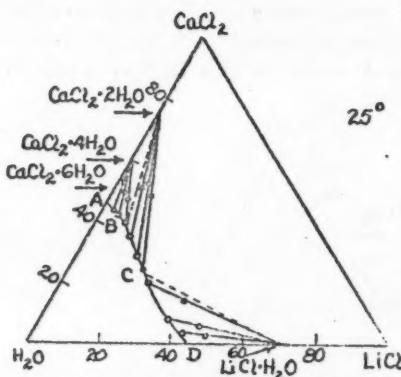


Fig. 2

TABLE 1

Amount (% by weight)			Total amt. of salts (% by weight)	Composition of solid phase (% by weight)		Solid phases
LiCl	BeCl ₂	H ₂ O		LiCl	BeCl ₂	
<u>25° Isotherm</u>						
45.95	—	54.05	45.95	—	—	
39.46	5.48	55.06	44.94	58.12	2.36	
37.07	7.92	55.01	44.99	56.60	3.17	
33.34	11.52	55.14	44.86	51.75	6.12	
25.27	18.66	56.13	43.87	45.94	10.08	$\text{LiCl} \cdot \text{H}_2\text{O}$
18.67	24.46	56.87	43.13	38.86	14.51	
15.63	27.41	56.96	43.04	36.43	18.20	
9.14	33.25	57.61	42.39	31.51	21.23	
6.20	36.07	57.73	42.27	—	—	
2.18	39.65	58.17	41.83	1.62	44.26	$\text{BeCl}_2 \cdot 4\text{H}_2\text{O}$
—	41.72	58.28	41.72	—	—	
<u>40° Isotherm</u>						
48.98	—	52.02	47.98	—	—	
40.86	6.48	52.66	47.34	58.92	2.51	
37.67	9.56	52.76	47.24	56.80	4.02	
30.75	16.12	53.13	46.87	51.16	8.49	$\text{LiCl} \cdot \text{H}_2\text{O}$
23.52	22.23	54.25	45.75	44.42	12.60	
15.53	30.14	54.33	45.67	39.51	17.47	
7.34	38.02	54.63	45.37	34.10	22.46	$\text{LiCl} \cdot \text{H}_2\text{O}$
5.22	39.86	54.92	45.08	23.55	29.88	
2.14	42.91	54.95	45.05	—	—	$\text{LiCl} \cdot \text{H}_2\text{O} + \text{BeCl}_2 \cdot 4\text{H}_2\text{O}$
—	44.12	55.88	44.12	—	—	$\text{BeCl}_2 \cdot 4\text{H}_2\text{O}$

When the results of Novoselova and Sosnovskaya [4] on the isotherm of the system at 0° are compared with ours, it will be seen that with rise in temperature, the curve (BC) for the crystallization of beryllium chloride is shortened and the curve (AB) for the crystallization of lithium chloride is correspondingly lengthened. Hence, the salting-out power of BeCl₂ with respect to LiCl increases with rise in temperature. Although lithium chloride in the systems LiCl-NaCl-H₂O and LiCl-KCl-H₂O, studied by us [7], has the role of a salting-out agent, it has no such significance in the present system. It should be pointed out that in the present system, no chemical compounds are formed, whereas the results of Schmidt [8] show that in the system LiCl-BeCl₂, in absence of solvent, a compound 2LiCl·BeCl₂ is formed, which melts with decomposition.

The 25° and 40° isotherms of the system LiCl-CaCl₂-H₂O (Table 2, Fig. 2). The formation of viscous solutions in this system made the taking of test samples and the attainment of equilibrium difficult. Aqueous solutions of calcium chloride have a strong tendency to exhibit supersaturation. Equilibrium was attained after three days; settling in the liquid phase required 1-3 hours, depending on the calcium chloride concentration. Solutions of appreciable lithium chloride content settled much more quickly.

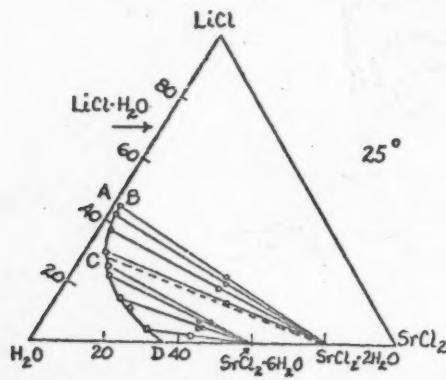


Fig. 3

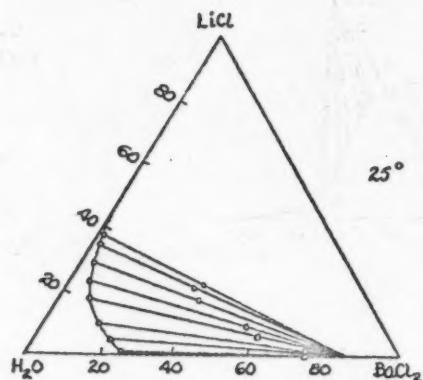


Fig. 4.

TABLE 2

LiCl	CaCl ₂	H ₂ O	Total amt. of salts (% by weight)	Composition of solid phase (% by weight)		Solid phase
				LiCl	CaCl ₂	
<u>25° Isotherm</u>						
45.98	—	54.02	45.98	—	—	
42.47	30.8	54.45	45.55	48.53	2.46	
36.66	8.02	55.32	44.68	45.44	5.21	
24.64	19.48	58.88	44.12	37.31	14.12	
20.51	24.72	54.77	45.23	11.02	48.15	
17.22	28.31	54.47	45.53	8.96	51.64	
12.13	34.97	52.90	47.10	7.68	50.31	
8.30	39.23	52.47	47.53	5.51	47.23	
5.45	41.62	52.93	47.07	3.44	49.54	
3.78	42.54	58.68	46.32	2.46	52.62	
—	46.15	53.85	46.15	—	—	
<u>40° Isotherm</u>						
47.98	—	52.02	47.98	—	—	
44.01	6.13	49.56	50.14	55.46	3.50	
39.08	12.12	48.80	51.20	52.59	7.03	
34.12	20.30	45.58	54.42	48.12	12.47	
29.46	27.58	42.96	57.04	43.80	18.81	
28.05	29.54	42.41	57.59	—	—	
26.63	30.82	42.55	57.45	17.24	46.58	
23.87	32.35	43.78	56.22	15.31	47.56	
17.48	38.06	44.46	55.54	13.17	47.94	
13.27	42.18	44.55	55.45	9.96	49.50	
5.41	50.19	44.40	55.60	5.04	52.76	
2.54	53.10	44.36	55.64	—	—	
1.67	54.20	44.13	55.87	1.48	55.31	
—	55.84	44.16	55.84	—	—	

TABLE 3

Point No.	Amount (% by weight)			Total amt. of salts (% by weight)	Composition of solid phase (% by weight)		Solid phase
	LiCl	SrCl ₂	H ₂ O		LiCl	SrCl ₂	
<u>25° Isotherm</u>							
1	45.95	—	54.05	45.95	—	—	
2	44.82	1.48	53.70	46.30	21.74	42.62	
3	41.54	2.36	56.10	43.90	19.88	43.86	
4	37.12	3.07	59.81	40.19	17.47	42.51	
5	29.48	4.95	65.57	34.43	13.23	47.02	
6	25.49	8.51	66.00	34.00	8.12	45.13	
7	22.51	10.62	66.87	33.13	7.98	42.18	
8	14.72	17.53	67.75	32.25	4.09	44.46	
9	11.89	21.14	66.97	33.03	3.50	44.37	
10	5.48	28.03	66.49	33.51	2.61	42.50	
11	—	36.79	63.21	36.79	—	—	
<u>40° Isotherm</u>							
1	47.98	—	52.02	47.98	—	—	
2	47.01	0.98	52.01	47.99	—	—	
3	46.22	1.65	52.13	47.87	29.04	31.48	
4	38.67	3.26	58.07	41.93	22.54	34.70	
5	31.73	5.84	62.43	37.57	17.25	37.82	
6	25.14	9.98	64.88	35.12	14.48	39.20	
7	17.80	19.25	62.95	37.05	6.60	44.06	
8	11.66	25.73	62.61	37.39	4.97	45.10	
9	5.05	32.12	61.83	38.17	2.61	47.54	
10	2.40	36.37	61.23	38.77	1.23	48.69	
11	—	40.12	59.88	40.12	—	—	

On Fig. 2, there are three curves: AB, the crystallization curve of $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$; BC, the crystallization curve of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and CD, the lithium chloride monohydrate curve. In spite of some precise work, the curve for $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ remained undetermined. These isotherms show quite clearly that in this system, LiCl plays the part of a dehydrating agent. For this and other systems the analytical results for the 40° isotherm were not plotted on the diagram, since they were completely analogous with respect to the crystallization of the respective components to the results for the 25° isotherm.

The 25° and 40° isotherms of the system $\text{LiCl}-\text{SiCl}_2-\text{H}_2\text{O}$ (Table 3, Fig. 3). Chemically, calcium chloride is similar to strontium chloride. The latter is of lower solubility and has fewer hydrates than CaCl_2 . In particular $\text{SrCl}_2 \cdot 4\text{H}_2\text{O}$ is not known. The solutions were not of high viscosity and did not show supersaturation, and settling in the liquid phase required only short periods of time. On Fig. 3 there are three curves: AB, the very short curve for the crystallization $\text{LiCl} \cdot \text{H}_2\text{O}$; BC, the crystallization curve of $\text{SrCl}_2 \cdot 2\text{H}_2\text{O}$ and CD, the $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ curve. In this system, lithium chloride dehydrates strontium chloride hexahydrate, which loses four molecules of water and is converted into the dihydrate; at the same time LiCl acts as a salting-out agent.

The 25° isotherm of the system $\text{LiCl}-\text{BaCl}_2-\text{H}_2\text{O}$ (Table 4, Fig. 4). This system was studied only at 25°, for at elevated temperatures lithium chloride is precipitated at moderate concentrations.

As will be seen from Fig. 4, in this system, we have only the crystallization curve of barium chloride. This is a feature of those systems in which one of the components acts as a powerful salting-out agent with respect to the other in various solvents. It was not found possible to determine the lithium chloride curve.

TABLE 4

LiCl	BaCl ₂	H ₂ O	Total amt. of salts (% by weight)	Composition of solid phase (% by weight)		Solid phases
				LiCl	BaCl ₂	
<u>25° Isotherm</u>						
45.95	—	54.05	45.95	—	—	$\text{LiCl} \cdot \text{H}_2\text{O}$
34.12	1.52	64.36	35.64	21.23	33.82	
28.91	3.02	68.07	31.93	17.64	36.48	
23.34	5.54	71.12	28.88	9.15	53.47	
17.48	8.28	74.24	25.76	6.04	58.54	
10.15	14.32	75.53	24.47	3.48	64.92	$\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$
5.16	20.13	74.71	25.29	1.03	71.06	
1.52	24.56	73.92	26.08	0.28	72.37	
—	26.75	73.25	26.75	—	—	

The 25° and 40° isotherms of the system $\text{LiCl}-\text{ZnCl}_2-\text{H}_2\text{O}$ (Table 5, Fig. 5). In this system, the establishment of equilibrium required a long time (3-4 days), and in the field of crystallization of zinc chloride the solid phase was a sirupy viscous mass.

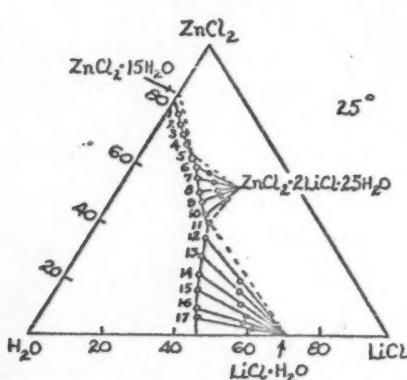


Fig. 5

It will be seen from Fig. 5 that the solubility isotherm for lithium and zinc chlorides consists of three curves: the first curve, from points 1-5, corresponds to the crystallization of $\text{ZnCl}_2 \cdot 1.5\text{H}_2\text{O}$. The composition of the solid phase for this curve coincided with that of the liquid phase, and the point for the composition of the solid phase was, therefore, not plotted. The principal solid phase points were recorded with the aid of a microscope. At point 5, at the limit for the formation of the chemical compound, complete solidification of the system was observed, similar to that observed at the eutectic points of systems at low temperature. At this point, the liquid phase was converted into a continuous gellike mass. Then, after addition of a small amount of saturated LiCl solution, separation of liquid and solid phases was observed. The second curve (points 6-10) corresponds to the compound $\text{ZnCl}_2 \cdot 2\text{LiCl} \cdot 2.5\text{H}_2\text{O}$. The tie-lines joining the points (6-10) for the solutions with those for the corresponding "dry" residues meet at the point for the true solid phase, which corresponds to the double salt indicated above. The solubility curve from point 11 to point 17 corresponds to the separation of lithium chloride monohydrate into the solid phase. The same three curves are found also at 40°.

TABLE 5

LiCl	ZnCl ₂	H ₂ O	Total amt. of salts (% by weight)	Composition of solid phase (% by weight)		Solid phases
				LiCl	ZnCl ₂	
<u>25° Isotherm</u>						
—	81.20	18.80	81.20	—	—	
3.65	76.18	20.17	79.83	3.58	76.21	
6.25	72.46	21.29	78.71	—	—	ZnCl ₂ · 1.5H ₂ O
9.10	68.23	22.67	77.33	9.40	68.34	
11.28	65.30	23.42	76.58	—	—	
14.71	60.62	24.67	75.33	15.17	61.89	ZnCl ₂ · 1.5H ₂ O + ZnCl ₂ · 2LiCl · 2.5H ₂ O
17.36	58.42	24.22	75.78	22.10	56.14	
20.05	53.86	26.09	73.91	25.07	52.53	
23.46	49.61	26.93	73.07	27.26	50.11	ZnCl ₂ · 2LiCl · 2.5H ₂ O
25.27	46.48	28.25	71.75	29.59	48.06	
29.12	41.40	29.48	70.52	30.71	46.12	
30.51	38.87	30.62	69.38	—	—	ZnCl ₂ · 2LiCl · 2.5H ₂ O + LiCl · H ₂ O
32.47	33.48	34.05	65.95	19.18	49.10	
34.60	27.20	38.20	61.80	15.10	50.92	
36.50	20.90	42.60	54.40	15.41	50.18	
39.19	15.18	45.63	54.37	6.89	56.46	LiCl · H ₂ O
41.43	9.17	49.40	50.60	4.53	57.15	
43.20	5.64	51.16	48.84	2.62	59.60	
45.95	—	54.05	45.95	—	—	
<u>40° Isotherm</u>						
—	81.86	18.14	81.86	—	—	
4.21	77.13	18.66	81.34	4.30	77.26	
10.46	69.50	20.04	79.96	10.26	69.71	ZnCl ₂
15.48	64.31	20.21	79.79	16.14	65.67	
19.56	60.07	20.37	79.63	20.12	61.10	ZnCl ₂ + ZnCl ₂ · 2LiCl · 2.5H ₂ O
20.62	57.48	21.90	78.10	27.18	54.50	ZnCl ₂ · 2LiCl · 2.5H ₂ O
29.60	43.42	26.98	73.02	—	—	ZnCl ₂ · 2LiCl · 2.5H ₂ O + LiCl · H ₂ O
30.16	39.60	30.24	69.76	47.13	23.32	
30.68	25.16	44.16	55.84	52.26	13.10	
41.65	12.90	45.45	54.55	59.34	4.62	
47.98	—	52.02	47.98	—	—	LiCl · H ₂ O

The compound obtained ZnCl₂ · 2LiCl · 2.5H₂O resembles crystals of the rhombic syngony in external habit (Fig. 6) [see plate, page 342] and is highly hygroscopic. It is difficult to dry out the crystals in a desiccator over sulfuric acid, or even over phosphoric anhydride; they readily dissolve in alcohol, and they readily hydrate in air. In order to confirm the composition of this compound, we prepared a synthetic solution corresponding approximately to the compound, and then evaporated it isothermally under reduced pressure. The first crystals that appeared were rapidly separated and dried in a desiccator over sulfuric acid. Analysis of the crystals gave the following results:

Found %: ZnCl₂ 50.56; LiCl 32.47; H₂O 16.97.
ZnCl₂ · 2LiCl · 2.5H₂O. Calculated %: ZnCl₂ 51.22; LiCl 31.87; H₂O 16.91.

The 40° isotherm confirmed the presence of the compound obtained at 25°. The solubility of lithium chloride changes very little in presence of increasing amounts of ZnCl₂ right up to the point at which the compound is formed.

The 25° and 40° isotherms of the system LiCl-CdCl₂-H₂O (Table 6, Fig. 7). Increase in the concentration of cadmium chloride led to rise in the viscosity of the solutions, and increase in the LiCl concentration of the solutions accelerated settling in the liquid phase. The same phenomenon occurred also in the preceding system. There are three curves in Fig. 7: AB, the crystallization curve for lithium chloride monohydrate; BC, the crystallization curve of the chemical compound LiCl · CdCl₂ · 2.5H₂O; and CD, the crystallization curve for the corresponding cadmium chloride hydrate. The length of the curve for the crystallization of the double compound is reduced at 40°.



Fig. 6.



Fig. 8

TABLE 6

LiCl	CdCl ₂	H ₂ O	Total amt. of salts (% by weight)	Composition of solid phase (% by weight)		Solid phases
				LiCl	CdCl ₂	
<u>25° Isotherm</u>						
45.95	—	54.05	45.95	—	—	
44.20	2.02	53.78	46.22	55.40	1.62	
42.31	6.48	51.21	48.79	53.54	3.25	$\left\{ \begin{array}{l} \text{LiCl} \cdot \text{H}_2\text{O} \\ \text{LiCl} \cdot \text{H}_2\text{O} + \text{LiCl} \cdot \text{CdCl}_2 \cdot 2.5\text{H}_2\text{O} \end{array} \right.$
41.43	9.63	48.94	51.06	53.26	5.24	
39.61	13.00	47.39	52.61	—	—	
37.60	15.14	47.26	52.74	26.12	44.38	
32.68	18.96	48.36	51.64	22.95	47.53	$\left\{ \begin{array}{l} \text{LiCl} \cdot \text{CdCl}_2 \cdot 2.5\text{H}_2\text{O} \\ \text{LiCl} \cdot \text{CdCl}_2 \cdot 2.5\text{H}_2\text{O} \end{array} \right.$
28.12	24.04	47.84	52.16	20.84	50.61	
25.07	27.80	47.13	52.87	21.16	50.47	
19.96	34.25	45.79	54.21	17.83	52.60	
17.40	37.68	44.92	55.08	16.10	55.37	$\left\{ \begin{array}{l} \text{LiCl} \cdot \text{CdCl}_2 \cdot 2.5\text{H}_2\text{O} \\ \text{LiCl} \cdot \text{CdCl}_2 \cdot 2.5\text{H}_2\text{O} \end{array} \right.$
14.28	42.55	43.17	56.83	15.48	56.86	
12.63	46.07	41.30	58.70	13.68	58.74	
10.54	49.12	40.34	59.66	—	—	$\left\{ \begin{array}{l} \text{CdCl}_2 \cdot 2.5\text{H}_2\text{O} + \text{LiCl} \cdot \text{CdCl}_2 \cdot 2.5\text{H}_2\text{O} \\ \text{CdCl}_2 \cdot 2.5\text{H}_2\text{O} \end{array} \right.$
7.20	52.51	40.29	59.71	4.10	66.15	
3.12	55.82	41.06	58.94	1.79	69.53	$\left\{ \begin{array}{l} \text{CdCl}_2 \cdot 2.5\text{H}_2\text{O} \\ \text{CdCl}_2 \cdot 2.5\text{H}_2\text{O} \end{array} \right.$
—	59.48	40.52	59.48	—	—	
<u>40° Isotherm</u>						
47.98	—	52.02	47.98	—	—	
45.35	4.26	50.39	49.61	56.23	2.50	$\left\{ \begin{array}{l} \text{LiCl} \cdot \text{H}_2\text{O} \\ \text{LiCl} \cdot \text{H}_2\text{O} + \text{LiCl} \cdot \text{CdCl}_2 \cdot 2.5\text{H}_2\text{O} \end{array} \right.$
39.74	15.30	44.96	55.04	54.05	8.22	
38.86	18.12	43.02	56.98	—	—	$\left\{ \begin{array}{l} \text{LiCl} \cdot \text{CdCl}_2 \cdot 2.5\text{H}_2\text{O} \\ \text{LiCl} \cdot \text{CdCl}_2 \cdot 2.5\text{H}_2\text{O} \end{array} \right.$
37.50	19.51	42.99	57.01	25.02	47.43	
28.13	28.39	43.48	56.52	20.18	53.07	
17.38	39.67	42.95	57.05	17.34	56.70	
15.57	42.20	42.23	57.77	—	—	$\left\{ \begin{array}{l} \text{CdCl}_2 \cdot \text{H}_2\text{O} + \text{LiCl} \cdot \text{CdCl}_2 \cdot 2.5\text{H}_2\text{O} \\ \text{CdCl}_2 \cdot \text{H}_2\text{O} \end{array} \right.$
13.08	45.15	41.77	58.23	5.43	71.48	
4.28	55.47	40.25	59.75	2.25	73.59	
—	62.14	37.86	62.14	—	—	

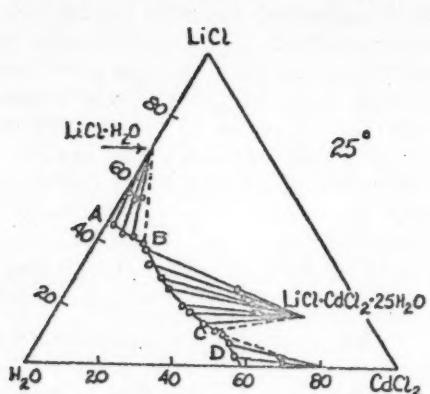


Fig. 7

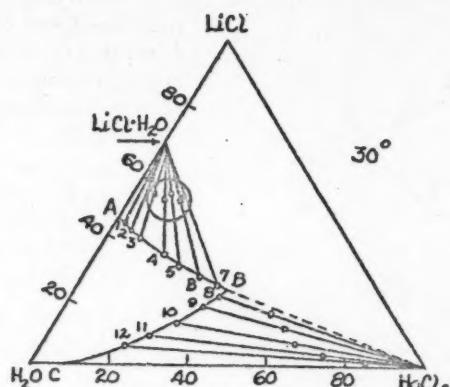


Fig. 9

By a method similar to that used for the preparation of crystals of $ZnCl_2 \cdot 2LiCl \cdot 2.5H_2O$ we prepared also some well formed clear crystals of the compound $LiCl \cdot CdCl_2 \cdot 2.5H_2O$ (Fig. 8), which were decomposed by alcohol to the component substances.

This compound decomposes when exposed to the air, but more slowly than the analogous zinc chloride compound. Analysis of the crystals gave the following results:

Found %: $LiCl$ 14.95; $CdCl_2$ 66.87; H_2O 18.22
 $LiCl \cdot CdCl_2 \cdot 2.5H_2O$. Calculated %: $LiCl$ 15.66; $CdCl_2$ 67.71; H_2O 16.63

In external habit, the crystals belong to the monoclinic syngony, which is characteristic for $CdCl_2 \cdot 2.5H_2O$.

The 30° isotherm of the system $LiCl - HgCl_2 - H_2O$ (Table 7, Fig. 9). The solubility of mercury halides in presence of chlorides of the alkali and alkaline earth metals has been studied by Herz and Paul [9]. These authors precipitated mercury ions with hydrogen sulfide. The chlorine was titrated with silver nitrate in presence of potassium chlomate as indicator. We have used this method of analysis, but obtained low results. We, therefore, preferred to carry out the analysis for mercury ions by Korenman's method [6] and determine chlorine only gravimetrically.

TABLE 7

LiCl	HgCl ₂	H ₂ O	Total amt. of salts (% by weight)	Composition of solid phase (% by weight)		Solid phases
				LiCl	HgCl ₂	
47.16	—	52.84	47.16	—	—	
44.05	2.53	53.42	46.58	57.83	1.46	
41.48	5.61	52.91	47.09	57.12	3.06	
38.47	9.62	51.91	48.09	53.16	5.54	
34.10	16.07	49.83	50.17	51.25	9.13	
30.39	22.50	47.11	52.89	53.28	10.20	
27.03	29.24	43.73	56.27	50.17	14.32	
23.90	36.08	40.02	59.98	52.18	15.74	
22.70	38.05	39.25	60.75	—	—	
21.66	37.80	40.54	59.46	16.47	53.06	
18.21	35.29	46.50	53.50	11.35	54.13	
14.07	31.22	54.71	45.29	7.60	63.54	
8.60	25.53	65.87	34.13	3.24	73.09	
5.36	21.75	72.89	27.11	1.86	84.47	
—	6.92	93.08	6.92	—	—	

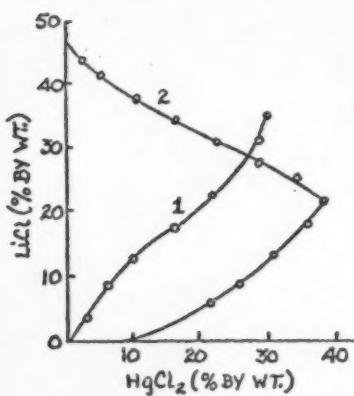


Fig. 10. 1) According to Herz and Paul at 25°; 2) according to our results at 30°.

According to Herz and Paul's results, the solubility of $HgCl_2$ rises from 2.65% to 30.62% at an $LiCl$ content of 35.27%. According to our results, the solubility of $HgCl_2$ rises from 6.92% to 38.05% at an $LiCl$ content of 22.70% in the solution. The rise in the solubility of $HgCl_2$ was found by these authors also in presence of halides of other alkali and alkaline earth metals, which may be explained by the formation of chemical compounds. We have carried out analyses on the liquid and solid phases, but have been unable to establish the formation of compounds. Herz and Paul point out that no complex salts were obtained in the solid phases. We consider that this anomalous solubility behavior can be explained by the formation of unstable complex compounds between $HgCl_2$ and metal chlorides in solution.

On Fig. 9, we have two curves: AB, the crystallization curve of lithium chloride; and BC, the crystallization curve of mercuric chloride. It was noteworthy that for points 3-7 floating of the solid phase occurred; after long stirring it gradually fell to the bottom of the reaction vessel. This is to be explained by the fact that the density of the solution was slightly higher than that of $LiCl$; thus, we found the density of the liquid phase for point 7 to be 2.077, and the density of $LiCl$ is 2.074.

Fig. 10 shows liquidus curves for the system $\text{LiCl}-\text{HgCl}_2-\text{H}_2\text{O}$. Curve 1 represents the results of Herz and Paul at 25°, and Curve 2 represents our results at 30°. As will be seen, the solubility of HgCl_2 increases with rise in temperature and increase in the concentration of LiCl up to a certain limit.

SUMMARY

1. Ternary aqueous systems containing lithium chloride and chlorides of Group II metals have been studied by the isothermal method.
2. In the systems $\text{LiCl}-\text{BeCl}_2-\text{H}_2\text{O}$, $\text{LiCl}-\text{CaCl}_2-\text{H}_2\text{O}$, $\text{LiCl}-\text{SrCl}_2-\text{H}_2\text{O}$ and $\text{LiCl}-\text{BaCl}_2-\text{H}_2\text{O}$, no chemical compounds are formed between the components.
3. In the systems $\text{LiCl}-\text{ZnCl}_2-\text{H}_2\text{O}$ and $\text{LiCl}-\text{CdCl}_2-\text{H}_2\text{O}$, the chemical compounds $\text{ZnCl}_2 \cdot 2\text{LiCl} \cdot 2.5\text{H}_2\text{O}$ and $\text{LiCl} \cdot \text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ have been found.
4. In the system $\text{LiCl}-\text{HgCl}_2-\text{H}_2\text{O}$ the solubility of HgCl_2 is enhanced in presence of LiCl . No chemical compounds between the components were found.

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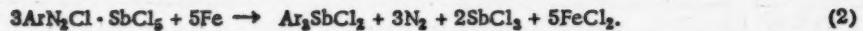
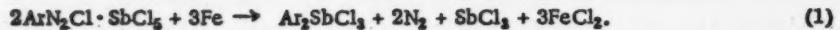
* See Consultants Bureau Translation, page 893.

SYNTHESIS OF ARYLSTIBONIC ACIDS VIA DOUBLE SALTS OF DIAZONIUM SALTS

AND ANTIMONY PENTACHLORIDE

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The double salts of diazonium salts and antimony pentachloride, which have been synthesized by one of us [1], can act as starting materials for the preparation of organoantimony compounds of various types. Thus it has been shown previously [2] that, when these double diazonium-antimony salts are decomposed with iron powder, high yields of compounds of the types Ar_2SbCl_3 and Ar_3SbCl_2 are obtained in accordance with the following equations:

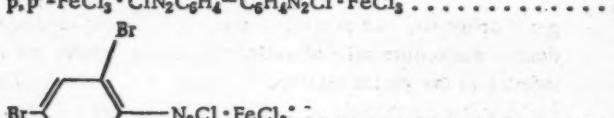
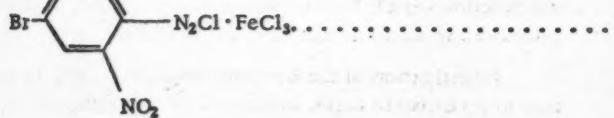


In the present investigation it has been shown that, when the double salts of diazonium salts and antimony pentachloride are decomposed with copper, arylstibonic acids are formed. The synthesis of arylstibonic acids was carried out in three stages: 1) preparation of the double diazonium salts of ferric chloride, 2) preparation of the double diazonium salts of antimony pentachloride, and 3) decomposition of the double diazonium salts of antimony pentachloride.

The preparation of the double diazonium salts of ferric chloride was carried out by the procedure developed by one of us and Kocheshkov [3], with small modifications indicated in the experimental part. Compounds of this type prepared for the first time are given in Table 1.

TABLE 1

Double Diazonium Salts of Ferric Chloride

Formula	M.P. (decomp.) (in. °C)	Color	Yield (%)
o-CH ₃ OC ₆ H ₄ N ₂ Cl · FeCl ₃	70	Yellow	54
p-CH ₃ OC ₆ H ₄ N ₂ Cl · FeCl ₃	78	"	63
o-C ₂ H ₅ OC ₆ H ₄ N ₂ Cl · FeCl ₃	56	"	45
p-C ₂ H ₅ OC ₆ H ₄ N ₂ Cl · FeCl ₃	40	"	67
2,4-(CH ₃) ₂ C ₆ H ₃ N ₂ Cl · FeCl ₃	45-46	"	80
p-CNSC ₆ H ₄ N ₂ Cl · FeCl ₃	88	"	30
α-C ₁₀ H ₇ N ₂ Cl · FeCl ₃	75-77	"	73
β-C ₁₀ H ₇ N ₂ Cl · FeCl ₃	78-79	"	87
p, p'-FeCl ₃ · ClN ₂ C ₆ H ₄ -C ₆ H ₄ N ₂ Cl · FeCl ₃	97-98	"	86
	84	"	95
	45-46	"	50
			

The synthesis of the double diazonium salts of antimony pentachloride was carried out by the procedure described by one of us [1]. The following double salts were obtained for the first time: the salts formed by antimony pentachloride with 2,4-dibromo-6-methylbenzenediazonium chloride (m.p. 138°, yield 93%), with p-methoxybenzenediazonium chloride (m.p. 129°, yield 59%), with o-ethoxybenzenediazonium chloride (m.p. 110°, yield 33%), and with p-ethoxybenzenediazonium chloride (m.p. 106°, yield 86%).

The decomposition of the double diazonium salts of antimony pentachloride was carried out in an acetone medium according to the equation:



The arylantimony tetrachloride was hydrolyzed with aqueous caustic soda and isolated in the form of the arylstibonic acid.

The effect of reaction conditions on the yield was investigated in detail in the case of the synthesis of phenylstibonic acid. The results of these experiments are given in Table 2.

TABLE 2

Effect of Reaction Conditions on the Yield of Phenylstibonic Acid

Amount of $\text{C}_6\text{H}_5\text{N}_2\text{Cl} \cdot \text{SbCl}_5$, in g	Amount of Cu_2Cl_2 , in g	Amount of solvent (ml)	Reaction temp. (°C)	Duration of reac- tion (hr.)	Yield of phenylstibonic acid	
					in g	(% of theoretical)
10	15	Acetone (100)	25	6	2.6	37
20	43	" (90)	25	44	2.4	17
5	20	" (60)	56	2	0.8	22
5	10	" (60)	25	4	1.2	34
5	10	Methanol (60)	30	24	0.25	7
5	8	Chloroform (100)	25	96	0.22	6
5	8	Glacial acetic acid (60)	25	(including 4 hrs. at 60)	0.1	3
5	8	Dioxane (50)	25	8	0.6	17
4.3	8	Methyl acetate (50)	25	5	1.2	39

It will be seen from Table 2 that the optimum conditions for the synthesis of phenylstibonic acid obtain when the double diazonium salt of antimony pentachloride is decomposed with a two- or three-fold excess of cuprous chloride at 25-30° for 4-5 hours in an acetone or methyl acetate medium.

The results of the syntheses of certain other arylstibonic acids [4] are given in Table 3 (the yields of the same substances prepared by Schmidt's reaction are given in parentheses).

TABLE 3

Yields of Arylstibonic Acids

Formula	Yield (% of theoretical amt.)
$\text{C}_6\text{H}_5\text{SbO}(\text{OH})_2$	39 (40-60)
$\text{p-CH}_3\text{C}_6\text{H}_4\text{SbO}(\text{OH})_2$	30 (40)
$2,4-(\text{CH}_3)_2\text{C}_6\text{H}_3\text{SbO}(\text{OH})_2$	14 -
$\text{o-O}_2\text{NC}_6\text{H}_4\text{SbO}(\text{OH})_2$	1 -
$\text{m-O}_2\text{NC}_6\text{H}_4\text{SbO}(\text{OH})_2$	6 -
$\text{p-O}_2\text{NC}_6\text{H}_4\text{SbO}(\text{OH})_2$	12 (11)
$\text{o-ClC}_6\text{H}_4\text{SbO}(\text{OH})_2$	1 -
$\text{p-ClC}_6\text{H}_4\text{SbO}(\text{OH})_2$	5 (38)
$\text{p-BrC}_6\text{H}_4\text{SbO}(\text{OH})_2$	1 (14)
$\text{p-IC}_6\text{H}_4\text{SbO}(\text{OH})_2$	9 (5)
$\text{p-CH}_3\text{OC}_6\text{H}_4\text{SbO}(\text{OH})_2$	4 (31)
$\text{o-C}_2\text{H}_5\text{OC}_6\text{H}_4\text{SbO}(\text{OH})_2$	4 -
$\text{p-C}_2\text{H}_5\text{OC}_6\text{H}_4\text{SbO}(\text{OH})_2$	3 -
$\alpha\text{-C}_10\text{H}_7\text{SbO}(\text{OH})_2$	4 -
$\beta\text{-C}_10\text{H}_7\text{SbO}(\text{OH})_2$	8 (2)

In a number of cases (phenyl-, p-tolyl-, p-iodophenyl-, p-nitrophenyl-, and 2-naphthyl-stibonic acids) this method of preparation by the decomposition of double diazonium salts of antimony pentachloride can compete successfully with Schmidt's method [5]. The yields of phenyl-, p-iodophenyl-, p-nitrophenyl-, and p-tolyl-stibonic acids, prepared via the double diazonium salts of antimony pentachloride, are not inferior to the yields attained by Schmidt's method. The yield of 2-naphthylstibonic acid prepared by the decomposition of $\text{ArN}_2\text{Cl} \cdot \text{SbCl}_5$ is four times as great as that of the same substance prepared by Schmidt's reaction. Moreover, in the synthesis of arylstibonic acids via $\text{ArN}_2\text{Cl} \cdot \text{SbCl}_5$, as opposed to the synthesis by Schmidt's method, copious foam formation does not occur (and there is, therefore, no need to use reaction vessels having enormous capacities), and precipitates causing difficult filtration are not formed.

Investigation of the by-products showed that, in addition to arylstibonic acids, substances in which the diazo group was replaced by halogen were formed. Thus, after decomposition

of the double salt of antimony pentachloride with p-iodobenzenediazonium chloride, 1-chloro-4-iodobenzene was isolated. In other cases, 1-chloro-2-nitrobenzene, 3,5-dibromo-2-chlorotoluene, etc., were isolated correspondingly. Formation of products of the replacement of the diazo group by hydrogen practically did not occur, a fact that allows us to infer that the reaction studied is of homolytic, not free-radical, character.

EXPERIMENTAL

1. Preparation of the Double Diazonium Salts of Ferric Chloride

The experiments were performed under the conditions indicated by Kocheshkov and Nesmeyanov [3], with slight modifications: the ferric chloride (three-fold excess) was dissolved in the minimum amount of water at 50-60°, and the solution was then cooled to -5° and poured into a cold solution of the diazotized amine. The double diazonium salt of ferric chloride was precipitated by addition of concentrated HCl to the stirred solution. With this procedure precipitation of the double salt readily occurred already at temperatures of 0-5°. The double salts so obtained were dried in the air and, when necessary, purified by reprecipitation from acetone with ether.

By means of this procedure the following double salts were prepared for the first time: the double salts of ferric chloride with o-methoxybenzenediazonium chloride (m.p. 70°, yield 54%), with p-methoxybenzenediazonium chloride (m.p. 78°, yield 63%), with o-ethoxybenzenediazonium chloride (m.p. 56°, yield 45%), with p-ethoxybenzenediazonium chloride (m.p. 40°, yield 67%), with 2,4-dimethylbenzenediazonium chloride (m.p. 45-46°, yield 80%), with p-thiocyanatobenzenediazonium chloride (m.p. 88°, yield 30%), with 2-naphthalenediazonium chloride (m.p. 75-77°, yield 73%), with 1-naphthalenediazonium chloride (m.p. 78-79°, yield 87%), with tetrazotized benzidine (m.p. 97-98°, yield 86%), with 2,4-dibromo-6-methylbenzenediazonium chloride (m.p. 84°, yield 95%), and with 2,4-dibromo-6-nitrobenzenediazonium chloride (m.p. 45-46°, yield 50%). All of these double salts are yellow crystalline substances that melt with decomposition (the double salt of ferric chloride with tetrazotized benzidine melts with an explosion). With a few exceptions, these substances are stable to storage in air for several weeks.

2. Preparation of the Double Diazonium Salts of Antimony Pentachloride

The preparation was carried out by the procedure developed by one of us [1]. The following substances have been synthesized for the first time:

Double salt of antimony pentachloride with 2,4-dibromo-6-methylbenzenediazonium chloride, yield 93%, colorless crystals, m.p. 138° with decomposition.

	Found %: N 4.91; 4.89
CH ₃ Br ₂ C ₆ H ₄ N ₂ Cl · SbCl ₅ .	Calculated %: N 4.57

Double salt of antimony pentachloride with p-methoxybenzenediazonium chloride, yield 59%, pinkish crystals, m.p. 129° with decomposition.

	Found %: N 6.53; 6.43
CH ₃ OC ₆ H ₄ N ₂ Cl · SbCl ₅ .	Calculated %: N 6.44

Double salt of antimony pentachloride with o-ethoxybenzenediazonium chloride, yield 33%, pinkish crystals, m.p. 110° with decomposition.

	Found %: N 6.25; 6.24
C ₂ H ₅ OC ₆ H ₄ N ₂ Cl · SbCl ₅ .	Calculated %: N 6.23

Double salt of antimony pentachloride with p-ethoxybenzenediazonium chloride, yield 86%, pinkish crystals, m.p. 106° with decomposition.

	Found %: N 6.07; 6.17
C ₂ H ₅ OC ₆ H ₄ N ₂ Cl · SbCl ₅ .	Calculated %: N 6.23

In the syntheses of the last three substances, certain complications arose: when attempts were made to precipitate the substance with ether under the usual conditions [1], no precipitate formed; instead, two layers were formed - an oily layer and an ethereal layer. The reaction mixture (both layers) was evaporated down under reduced pressure, and the dry residue was reprecipitated from acetone with ether in order to purify it from ferric chloride. In the case of the double salts containing alkoxyphenyl radicals, still purer products were obtained by reprecipitation from methanol with concentrated hydrochloric acid.

3. Synthesis of Arylstibonic Acids

Synthesis of Phenylstibonic Acid. a) The double salt of benzenediazonium chloride 10 g (0.0228 mole) was mixed with cuprous chloride 15 g (0.09 mole). The mixture was placed in a flask, 100 ml of acetone* was added, and the contents were stirred for six hours at 25°. The solvent was distilled off, and the residue was ground with 80 ml of 5 N NaOH. After two hours, the insoluble residue was filtered off and washed with 5 N NaOH. The filtrate was acidified to Congo red with 5 N HCl. The precipitated phenylstibonic acid was filtered off, washed well with water, and dried at 80-90° (yield 2.6 g, i.e., 37%). The substance was dissolved in concentrated hydrochloric acid and converted by addition of a solution of pyridine in hydrochloric acid into the pyridine complex $C_6H_5SbCl_4 \cdot C_5H_5N \cdot HCl$, m.p. 133° (after crystallization from alcohol) (the literature [6] gives m.p. 139°).

Found %: N 3.40; 3.42

$C_6H_5SbCl_4 \cdot C_5H_5N \cdot HCl$. Calculated %: N 3.07

The phenylstibonic acid was converted also into the quinoline complex, which melted at 207° after crystallization from alcohol.

Found %: N 2.98; 3.09

$C_6H_5SbCl_4 \cdot C_9H_7N \cdot HCl$. Calculated %: N 2.77

b) When the reaction was carried out between 20 g (0.0456 mole) of the double salt of benzenediazonium chloride with antimony tetrachloride and 43 g (0.217 mole) of cuprous chloride in 90 ml of acetone at 25° for 44 hours, 2.4 g (17%) of phenylstibonic acid was obtained.

c) When 5 g (0.0114 mole) of the double salt of benzenediazonium chloride with antimony pentachloride was decomposed with 20 g (0.1 mole) of cuprous chloride in 60 ml of acetone at 56° for two hours, 0.8 g (22%) of phenylstibonic acid was obtained.

d) When 5 g (0.0114 mole) of the double salt of benzenediazonium chloride with antimony pentachloride was decomposed with 10 g (0.05 mole) of cuprous chloride in 60 ml of acetone at 25° for four hours, 1.2 g (34%) of phenylstibonic acid was obtained.

e) When 5 g (0.0114 mole) of the double salt of benzenediazonium chloride with antimony pentachloride was decomposed with 10 g (0.05 mole) of cuprous chloride in 60 ml of methanol at 30° for 24 hours, 0.25 g (7%) of phenylstibonic acid was obtained.

f) When 5 g (0.0114 mole) of the double salt was decomposed with 8 g (0.04 mole) of cuprous chloride in 100 ml of chloroform at 25° for 96 hours, 0.22 g (6%) of phenylstibonic acid was obtained.

g) When 5 g (0.0114 mole) of the double salt was decomposed with 8 g (0.04 mole) of cuprous chloride in 60 ml of glacial acetic acid for 92 hours at 25° and then for four hours at 60°, 0.1 g (3%) of phenylstibonic acid was obtained.

h) When 5 g (0.0114 mole) of the double salt was decomposed with 8 g (0.04 mole) of cuprous chloride in 50 ml of dioxane at 25° for eight hours, 0.6 g (17%) of phenylstibonic acid was obtained.

i) When 4.3 g (0.0098 mole) of the double salt was decomposed with 8 g (0.04 mole) of cuprous chloride in 50 ml of methyl acetate at 25° for five hours, 1.2 g (39%) of phenylstibonic acid was obtained.

Synthesis of p-Tolylstibonic Acid. a) The double salt of p-toluenediazonium chloride with antimony pentachloride 3.5 g (0.0077 mole) was decomposed with 7 g (0.035 mole) of cuprous chloride in 75 ml of acetone at 25° for six hours. The solvent was distilled off, and the residue was ground with 35 ml of 5 N NaOH. After two hours, the undissolved residue was filtered off and washed with 5 N NaOH. The filtrate was acidified to Congo red with 5 N HCl. The precipitated p-tolylstibonic acid was filtered off, well-washed with water, and dried at 70-80°. (Yield 0.65 g, i.e., 26%).

The p-tolylstibonic acid was converted into the pyridine complex, which melted, after crystallization from alcohol, at 176-178° (the literature [6] gives 180°).

Found %: N 3.03; 3.00

$CH_3C_6H_4SbCl_4 \cdot C_5H_5N \cdot HCl$. Calculated %: N 2.90

b) When 5 g (0.011 mole) of the double salt of p-toluenediazonium chloride with antimony pentachloride was decomposed with 9 g (0.045 mole) of cuprous chloride in 75 ml acetone at 56° for three hours, only traces of

* Once-distilled commercial acetone was used.

p-tolylstibonic acid were obtained.

c) When 5 g (0.011 mole) of the double salt of p-toluenediazonium chloride with antimony pentachloride was decomposed with 9 g (0.045 mole) of cuprous chloride in 50 ml of methyl acetate at 25° for five hours, 1.1 g (30%) of p-tolylstibonic acid was obtained.

Synthesis of p-Nitrophenylstibonic Acid. a) When 2.8 g (0.0058 mole) of the double salt of p-nitrobenzenediazonium chloride with antimony pentachloride was treated as in the previous experiments with 8 g (0.04 mole) of cuprous chloride in 60 ml of acetone at 56° for two hours, 0.25 g (12%) of p-nitrophenylstibonic acid was obtained. The stibonic acid was converted into its pyridine complex, which melted, after two crystallizations from alcohol, at 167-168° (the literature [6] gives 168.5°).

Found %: N 5.70; 5.52

$O_2NC_6H_4SbCl_4 \cdot C_5H_5N \cdot HCl$. Calculated %: N 5.59

b) When 5 g (0.01 mole) of the double salt of p-nitrobenzenediazonium chloride with antimony pentachloride was decomposed with 8 g (0.04 mole) of cuprous chloride in 50 ml of acetone at 25° for five hours, 0.15 g (4%) of p-nitrophenylstibonic acid was obtained.

Synthesis of m-Nitrophenylstibonic Acid. When 10 g (0.02 mole) of the double salt of m-nitrobenzenediazonium chloride with antimony pentachloride was decomposed with 6 g (0.03 mole) of cuprous chloride in 60 ml of acetone at 25° for 14 hours, 0.47 g (6%) of m-nitrophenylstibonic acid was obtained. The stibonic acid was converted into its pyridine complex, which melted, after two crystallizations from alcohol, at 187° (the literature [6] gives 187°).

Synthesis of o-Nitrophenylstibonic Acid. When 17.7 g (0.036 mole) of the double salt of o-nitrobenzenediazonium chloride with antimony pentachloride was decomposed with 22.3 g (0.13 mole) of cuprous chloride in 80 ml of acetone at 25° for six hours, 0.1 g (1.0%) of o-nitrophenylstibonic acid was obtained. The residue obtained after treatment of the reaction mixture with alkali and removal of the alkaline solution of the stibonic acid by filtration was dried and thoroughly extracted with ether. The ether extract was dried with calcium chloride, and the ether was evaporated off. The residue was 1-chloro-2-nitrobenzene; m.p. after recrystallization from alcohol 31° (the literature [7] gives 32.5°).

Synthesis of p-Chlorophenylstibonic Acid. When 10 g (0.025 mole) of the double salt of p-chlorobenzenediazonium chloride with antimony pentachloride was decomposed with 15 g (0.09 mole) of cuprous chloride in 60 ml of acetone at 25° for six hours, 0.35 g (5%) of p-chlorophenylstibonic acid was obtained.

Synthesis of o-Chlorophenylstibonic Acid. When 5.2 g (0.013 mole) of the double salt of o-chlorobenzenediazonium chloride with antimony pentachloride was decomposed with 8 g (0.04 mole) of cuprous chloride in 50 ml of acetone at 25° for six hours, 0.05 g (1%) of o-chlorophenylstibonic acid was obtained.

Synthesis of p-Bromophenylstibonic Acid. When 5 g (0.011 mole) of the double salt of p-bromobenzenediazonium chloride with antimony pentachloride was decomposed with 7 g (0.035 mole) of cuprous chloride in 50 ml of acetone at 25° for six hours, 0.05 g (1%) of p-bromophenylstibonic acid was obtained.

Synthesis of p-Iodophenylstibonic Acid. When 10 g (0.02 mole) of the double salt of p-iodobenzenediazonium chloride with antimony pentachloride was decomposed with 15 g (0.075 mole) of cuprous chloride in 60 ml of acetone at 25° for six hours, 0.75 g (9%) of p-iodophenylstibonic acid was obtained. The residue obtained after treatment of the reaction mixture with alkali and removal of the alkaline solution of the stibonic acid by filtration was extracted three times with 30-ml portions of ether. The ether solution was dried with calcium chloride, and the ether was evaporated off. The residue, 1-chloro-4-iodobenzene, was recrystallized from alcohol; m.p. 54° (the literature [8] gives 56°). The yield was 1.2 g (28%).

Synthesis of p-Methoxyphenylstibonic Acid. When 5 g (0.013 mole) of the double salt of p-methoxybenzenediazonium chloride with antimony pentachloride was decomposed with 7 g (0.035 mole) of cuprous chloride in 50 ml of acetone at 25° for six hours, 0.15 g (4%) of p-methoxyphenylstibonic acid was obtained.

Synthesis of p-Ethoxyphenylstibonic Acid. When 15 g (0.038 mole) of the double salt of p-ethoxybenzenediazonium chloride with antimony pentachloride was decomposed with 12 g (0.06 mole) of cuprous chloride in 80 ml of acetone at 25° for five hours, 0.3 g (3%) of p-ethoxyphenylstibonic acid was obtained.

Synthesis of o-Ethoxyphenylstibonic Acid. When 5 g (0.013 mole) of the double salt of o-ethoxybenzenediazonium chloride with antimony pentachloride was decomposed with 7 g (0.035 mole) of cuprous chloride in 50 ml of acetone at 25° for six hours, 0.15 g (4%) of o-ethoxyphenylstibonic acid was obtained.

Synthesis of 2,4-Dimethylphenylstibonic Acid. When 7.5 g (0.024 mole) of the double salt of 2,4-dimethylbenzenediazonium chloride with antimony pentachloride was decomposed with 6 g (0.03 mole) of cuprous chloride in 60 ml of acetone at 25° for eight hours, 0.75 g (14%) of 2,4-dimethylphenylstibonic acid was obtained.

Synthesis of 1-Naphthylstibonic Acid. When 3.5 g (0.007 mole) of the double salt of 1-naphthalenediazonium chloride with antimony pentachloride was decomposed with 3 g (0.015 mole) in 50 ml of acetone at 25° for five hours, 0.1 g (4%) of 1-naphthylstibonic acid was obtained. The 1-naphthylstibonic acid was converted into its pyridine complex, pale-yellow crystals of m.p. 186-188° (the literature [9] gives 187-189°).

Synthesis of 2-Naphthylstibonic Acid. a) When 3 g (0.006 mole) of the double salt of 2-naphthalenediazonium chloride with antimony pentachloride was decomposed with 5 g (0.025 mole) of cuprous chloride in 50 ml of acetone at 25° for four hours, and the reaction mixture was treated in the usual way, 0.18 g (8%) of 2-naphthylstibonic acid was obtained. The 2-naphthylstibonic acid was converted in the usual way into its pyridine complex $C_{18}H_7SbCl_4 \cdot C_5H_5N \cdot HCl$, which, after being crystallized from alcohol, was a yellow substance of m.p. 199-200° (according to the literature [9] it is a yellow substance, m.p. 200-202°).

Found %: N 2.75; 2.74

$C_{18}H_7SbCl_4 \cdot C_5H_5N \cdot HCl$. Calculated %: N 2.76

2-Naphthylstibonic acid was converted also into its quinoline complex, which, after being crystallized from alcohol, was a yellow substance, m.p. 183° with decomposition (according to the literature [9] it is a yellow substance, m.p. 174-176° with decomposition).

Found %: C 41.24; 41.24; H 3.05; 3.04; N 2.72; 2.60

$C_{18}H_7SbCl_4 \cdot C_9H_7N \cdot HCl$. Calculated %: C 41.00 H 2.70; N 2.52

b) When 5.3 g (0.0108 mole) of the double salt of 2-naphthalenediazonium chloride was decomposed with 9 g (0.045 mole) of cuprous chloride in 50 ml of methyl acetate at 25° for nine hours, 0.3 g (7%) of 2-naphthylstibonic acid was obtained.

Decomposition of the Double Salt of 2,4-Dibromo-6-methylbenzenediazonium Chloride with Antimony Pentachloride by means of Cuprous Chloride. When 10.0 g of the double salt of 2,4-dibromo-6-methylbenzenediazonium chloride with antimony pentachloride was decomposed with excess of cuprous chloride, the corresponding arylstibonic acid was not formed. Treatment of the reaction mixture as in the preceding experiment yielded 0.8 g of 3,5-dibromo-2-chlorotoluene as colorless crystals of m.p. 53°, soluble in ether, alcohol, and acetone.

Found %: C 29.22; H 1.74

$CH_3C_6H_2Br_2Cl$. Calculated %: C 29.45; H 1.75

This substance is described for the first time.

SUMMARY

1. A study has been made of the decomposition, in an organic medium in presence of cuprous chloride, of the double salts formed by diazonium salts with antimony pentachloride; the reaction results in the formation of arylstibonic acids.

2. In a number of cases (phenyl-, p-tolyl-, p-nitrophenyl-, p-iodophenyl-, and 2-naphthyl-stibonic acids) this reaction can successfully compete with the Bart-Schmidt-Scheller method for the synthesis of arylstibonic acids.

3. The nature of the by-products of the reaction indicates that the process is of a homolytic, not free-radical, character.

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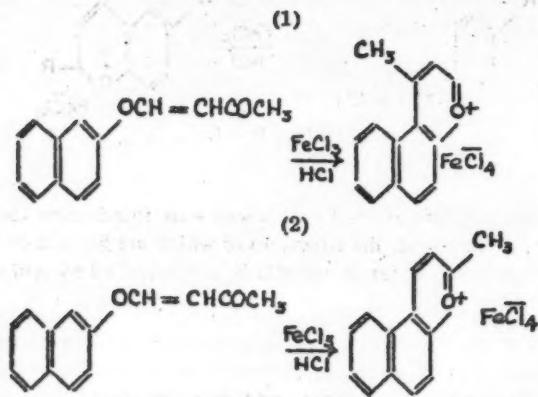
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REARRANGEMENT OF 2-PHENOXYVINYL KETONES

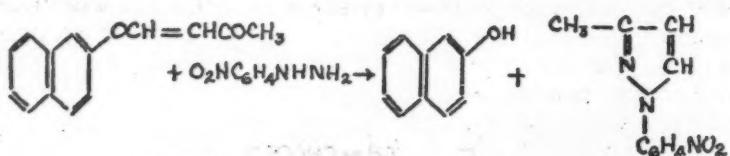
A. N. Nesmeyanov, N. K. Kochetkov, and M. I. Rybinskaya

By the action of phenols on 2-chlorovinyl ketones in an alkaline medium, we have recently [1] prepared 2-phenoxyvinyl ketones, the properties of which have received very little study. In this paper, we describe one of the reactions of 2-phenoxyvinyl ketones, which occurs when they are treated with ferric chloride or similar reagent.

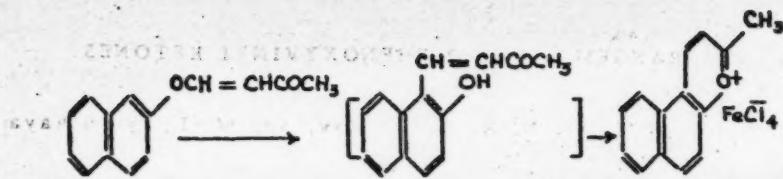
As we wished to extend the new medium for the synthesis of pyrylium salts that we have recently developed [2], we have studied the reaction of 2-phenoxyvinyl ketones with ferric chloride in the hope of obtaining naphtho- and benzo-pyrylium salts having a radical in the 4-position of the pyrylium ring. When methyl 2-(2-naphthoxy)vinyl ketone [4-(2-naphthoxy)-3-buten-2-one] was treated with ferric chloride in a mixture of hydrochloric and acetic acids, a methylnaphthopyrylium chloroferrate (III) was indeed formed. It was found unexpectedly, however, that the substance obtained was not a 1-methylnaphtho[2,1-b]pyrylium salt, but was 3-methylnaphtho[2,1-b]pyrylium chloroferrate (III), a fact that was established by comparison of the substance obtained with an authentic sample of the 3-methylnaphtho[2,1-b]pyrylium salt, the structure of which we have already established [2]. Hence, the reaction of methyl 2-(2-naphthoxy)vinyl ketone with ferric chloride proceeds not by Scheme 1, but by Scheme 2:



The structure of the original methyl 2-(2-naphthoxy)vinyl ketone is not in doubt, since on reaction with *p*-nitrophenylhydrazine it yields 2-naphthol and 3-methyl-1-(*p*-nitrophenyl)pyrazole:

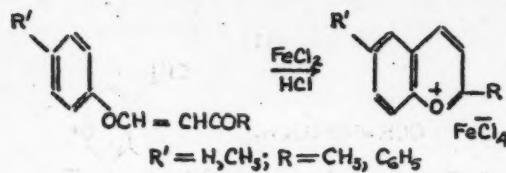


The result obtained in the reaction of the naphthoxyvinyl ketone with ferric chloride can be understood only on the assumption that, under the conditions of the reaction, there is initially a migration of the 3-oxo-1-alkenyl group from the oxygen to the carbon in the 1-position of the naphthalene nucleus, the intermediately formed 2-(2-hydroxy-1-naphthyl)vinyl methyl ketone then undergoing cyclization:



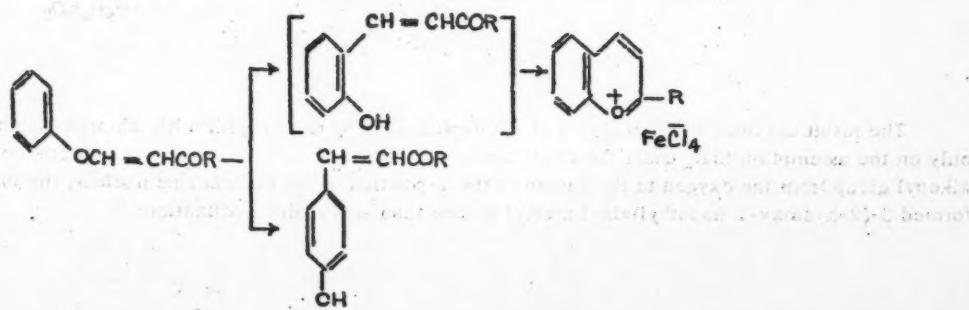
This rearrangement is reminiscent in its character of the well-known Fries rearrangement. This resemblance is in accord with the fact that, formally, 2-phenoxyvinyl ketones are so-called "vinylogs" of phenol esters, and from this point of view the reaction here described presents a new and interesting example of "vinylogy".

As further investigation has shown, the reaction is a fairly general one. Thus, when 2-(2-naphthoxy)vinyl propyl ketone [1-(2-naphthoxy)-1-hexen-3-one], which was synthesized by the general method for the preparation of phenoxyvinyl ketones already described [1], was treated with ferric chloride, a high yield of 3-propynaphtho[2,1-b]pyrylium chloroferrate (III) was obtained. Under the same conditions, i.e., in presence of ferric chloride in a mixture of hydrochloric and acetic acids, phenoxyvinyl ketones of the benzene series are also converted into pyrylium salts. We verified this in the case of the rearrangements of methyl 2-phenoxyvinyl ketone (4-phenoxy-3-buten-2-one) and methyl 2-p-tolyloxyvinyl ketone (4-p-tolyloxy-3-buten-2-one), and also of 2-phenoxyvinyl phenyl ketone (2-phenoxyacrylophenone), which was prepared by the action of phenol on 2-chlorovinyl phenyl ketone (2-chloroacrylophenone):

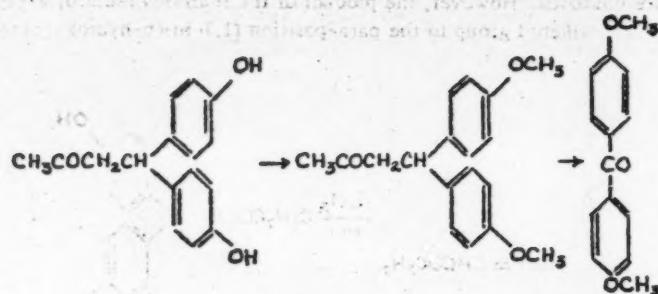


The benzopyrylium chloroferrates obtained in this way were found to be identical with disubstituted benzopyrylium salts obtained by another method, the structures of which are beyond doubt. In this case also, therefore, the reaction of phenoxyvinyl ketones with ferric chloride is accompanied by preliminary migration of the 3-oxo-1-alkenyl group into the aromatic nucleus.

We have further found that the yields of the pyrylium salts obtained by the rearrangement of methyl 2-(2-naphthoxy)vinyl ketone and methyl 2-p-tolyloxyvinyl ketone are fairly high (94% and 56% respectively), whereas treatment of methyl 2-phenoxyvinyl ketone and 2-phenoxyvinyl phenyl ketone with ferric chloride gave only low yields (11.8% and 10%) of pyrylium salts. It is known that in the Fries rearrangement the acyl group may migrate either to the ortho or to the para position. It will be clear that, for the 3-oxo-1-alkenyl group also, migration both to the ortho and to the para position is possible. It is to be expected, therefore, that for methyl 2-(2-naphthoxy)vinyl ketone and methyl 2-p-tolyloxyvinyl ketone, which have no free para positions, the only possibility is the formation of the ortho isomer, which will cyclize to a pyrylium salt, which is actually obtained in fairly high yield in these cases. On the other hand, in the case of methyl 2-phenoxyvinyl ketone and 2-phenoxyvinyl phenyl ketone, the formation of an ortho isomer is only one of the two possible directions that the reaction can take, and the yield of pyrylium salt is, therefore, less:

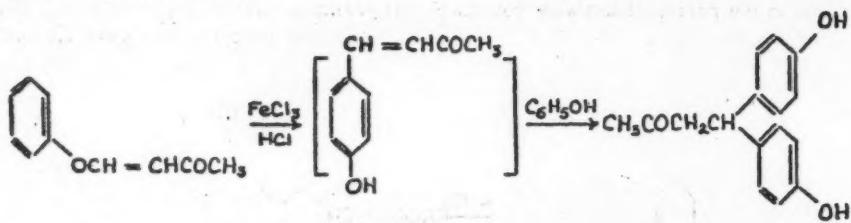


If this hypothesis is correct, then in the reaction of the two last compounds with ferric chloride we may expect the formation of the corresponding para-substituted styryl ketones. Actually, when methyl 2-phenoxyvinyl ketone reacted with ferric chloride, the reaction mixture yielded not only the pyrylium salt, but also a crystalline substance of m.p. 187°, which had the properties of a phenol. This compound, however, gave no reaction for a double bond and its melting point did not agree with that of 4-(p-hydroxyphenyl)-3-buten-2-one [3]. We established that this substance was the product of the further reaction of 4-(p-hydroxyphenyl)-3-buten-2-one under the conditions employed, and was 4,4'-bis(p-hydroxyphenyl)-2-butanone. The structure of this substance was proved by methylation with dimethyl sulfate or methyl iodide and subsequent oxidation of the resulting dimethyl ether with permanganate, which yielded 4,4'-dimethoxybenzophenone:

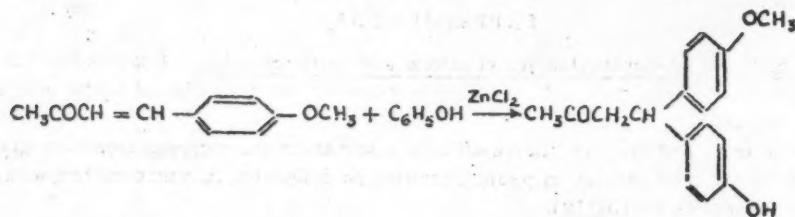


In the methylation, the monomethyl ether [4-(p-hydroxyphenyl)-4-(p-methoxyphenyl)-2-butanone] was isolated also.

The explanation of the formation of 4,4'-bis(p-hydroxyphenyl)-2-butanone when 2-chlorovinyl phenyl ketone is treated with ferric chloride must be that the 4-(p-hydroxyphenyl)-3-buten-2-one formed unites with a further molecule of phenol, which is constantly present in the reaction mixture owing to the partial splitting of the phenoxyvinyl ketone in an acid medium:



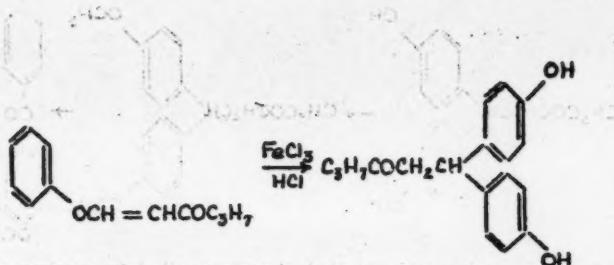
This hypothesis, which was based on known analogies from the literature [4, 5] was further confirmed by direct experiment. It was found that 4-(p-methoxyphenyl)-3-buten-2-one unites with one molecule of phenol in presence of zinc chloride, forming 4-(p-hydroxyphenyl)-4-(p-methoxyphenyl)-2-butanone, identical with the substance obtained by the methylation of 4,4'-bis(p-hydroxyphenyl)-3-buten-2-one:



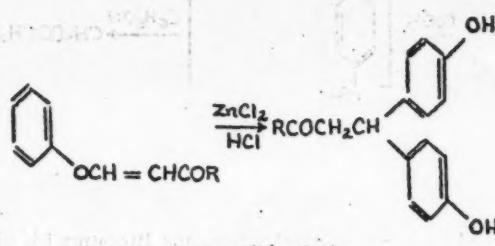
At the same time this confirmed the possibility of the addition of a molecule of phenol at the double bond of an α,β -unsaturated ketone in presence of such a mild agent as zinc chloride.

In the rearrangement of methyl 2-phenoxyvinyl ketone, therefore, we have succeeded in isolating not only the pyrylium salt formed as a result of the migration of the 3-oxo-1-alkenyl group to the ortho-position of the aromatic nucleus, but also a substance corresponding to migration to the para-position. A compound of the same type, 3,3-bis(p-hydroxyphenyl)propiophenone, was isolated together with the corresponding pyrylium salt in the rearrangement of 2-phenoxyvinyl phenyl ketone.

In the rearrangement of 2-phenoxyvinyl propyl ketone (1-phenoxy-1-hexen-3-one) in presence of ferric chloride, it was not found possible to isolate a pyrylium salt, owing to the extremely low stability of 2-alkyl-1-benzopyrylium salts containing the higher radicals. It is known, for example, that in an attempt to synthesize 2-ethyl-1-benzopyrylium chloroferrante (III) Decker [6] isolated a substance that decomposed completely in two hours, as a result of which he was unable to obtain it in an analytically pure form. 2-Alkyl-1-benzopyrylium salts having heavier radicals are unknown. However, the product of the rearrangement of 2-phenoxyvinyl propyl ketone with migration of the 3-oxo-1-alkenyl group to the para-position [1,1-bis(p-hydroxyphenyl)-3-hexanone] was isolated:



The similarity between this rearrangement and the Fried rearrangement is further confirmed by the fact that ferric chloride is not the only agent promoting the reaction. It was found that, when phenoxyvinyl ketones having a free para-position in the aromatic nucleus were treated with zinc chloride in hydrochloric acid, products formed by migration to the para-position were obtained. For example, methyl 2-phenoxyvinyl ketone gave 4,4-bis(p-hydroxyphenyl)-2-butanone in about 20% yield, and 2-phenoxyvinyl propyl ketone gave 1,1-bis(p-hydroxyphenyl)-3-hexanone:



It should be emphasized, however, that the rearrangement of phenoxyvinyl ketones occurs only in aqueous hydrochloric acid and cannot be effected at all in inert solvents, such as are normally used for the Fries rearrangement.

EXPERIMENTAL

1. Reaction of methyl 2-(2-naphthoxy)vinyl ketone with ferric chloride. A solution of 1.0 g of methyl 2-(2-naphthoxy)vinyl ketone [4-(2-naphthoxy)-3-buten-2-one] in 12 ml of glacial acetic acid was mixed with a solution of 5.0 g of anhydrous ferric chloride in concentrated hydrochloric acid. After a few minutes a yellow crystalline precipitate formed, and this was filtered off after a few hours and recrystallized from glacial acetic acid, yielding 1.7 g (90%) of green needles, m.p. 152°, showing no depression in a mixture test with 3-methyl-naphtho[2,1-b]pyrylium chloroferrate (III) [2].

2. Reaction of methyl 2-(2-naphthoxy)vinyl ketone with p-nitrophenylhydrazine. A solution of 0.27 g of methyl 2-(2-naphthoxy)vinyl ketone and 0.2 g of p-nitrophenylhydrazine in 10 ml of glacial acetic acid was heated to the boil and then set aside for one day at room temperature. The precipitated crystals were filtered off and recrystallized from glacial acetic acid, yielding 0.25 g (8%) of brown needles, m.p. 165-166°, showing no

depression in a mixture test with 3-methyl-1-(p-nitrophenyl)pyrazole. To the filtrate 30 ml of water and 20 ml of 20% caustic soda solution were added, and the solution was filtered and acidified with 20% sulfuric acid. The resulting precipitate was filtered off and recrystallized from aqueous alcohol, yielding 0.17 g (85%) of colorless crystals, m.p. 120°, showing no depression in a mixture test with 2-naphthol.

3. Preparation of 2-(2-naphthoxy)vinyl propyl ketone. To a vigorously stirred solution of 16.0 g of 2-naphthol in 50 ml of 10% caustic soda, 14.0 g of 2-chlorovinyl propyl ketone (1-chloro-1-hexen-3-one) was added dropwise; the reaction mixture was stirred for five hours and then set aside overnight. Water (250 ml) was then added, and the mixture was extracted with ether. The extract was dried over sodium sulfate, the solvent was distilled off, and the residue was vacuum-distilled, the fraction of b.p. 182-186° (4 mm) being collected (11.0 g, i.e., 51.3%). After redistillation the 2-(2-naphthoxy)vinyl propyl ketone [1-(2-naphthoxy)-1-hexen-3-one] was obtained as a yellowish oil, b.p. 184-186° (4 mm), n_D^{20} 1.6038.

Found %: C 79.78; 79.94; H 7.02; 6.94
 $C_{16}H_{18}O_2$. Calculated %: C 79.98; H 6.71.

4. Reaction of 2-(2-Naphthoxy)vinyl Propyl Ketone with Ferric Chloride. A solution of 1.0 g of 2-(2-naphthoxy)vinyl propyl ketone in 12 ml of glacial acetic acid was mixed with a solution of 5.0 g of ferric chloride in concentrated hydrochloric acid. A crystalline precipitate quickly made its appearance, and after four hours it was filtered off and recrystallized from glacial acetic acid, yielding 1.52 g (85.7 %) of light-green crystals, m.p. 124°, showing no depression in a mixture test with 3-propynaphtho[2,1-b]pyrylium chloroferrate (III).

5. Reaction of Methyl 2-Phenoxyvinyl Ketone with Ferric Chloride. A solution of 40 g of anhydrous ferric chloride in 60 ml of concentrated hydrochloric acid was added to a solution of methyl 2-phenoxyvinyl ketone (4-phenoxy-3-buten-2-one) in 80 ml of glacial acetic acid. The reaction mixture immediately became crimson in color, and after a few hours a red crystalline precipitate formed and was filtered off. Recrystallization from glacial acetic acid yielded 5.0 g (11.8%) of crimson needles, m.p. 125°, showing no depression in a mixture test with 2-methyl-1-benzopyrylium chloroferrate (III)[2]. To the filtrate from the separation of the 2-methyl-1-benzopyrylium chloroferrate (III) an equal volume of ether was added. The solution was repeatedly washed with water to remove ferric chloride, the process being continued until the aqueous layer ceased to become colored. The ether layer was then separated, and the ether was distilled off; the resinous residue was repeatedly extracted with boiling water. When the aqueous extracts were cooled, a crystalline precipitate appeared, and was filtered off and dissolved in 5% caustic soda to remove undissolved triacetylbenzene (0.2 g). The alkaline filtrate was acidified with 20% hydrochloric acid, and the resulting precipitate was filtered off. Recrystallization from water yielded 3.1 g (19.7%) of colorless needles, m.p. 187°.

Found %: C 75.10; 74.98; H 6.47; 6.29
 $C_{16}H_{16}O_3$. Calculated %: C 75.00; H 6.25

4,4-Bis(p-hydroxyphenyl)-2-butanone is readily soluble in ether, acetone, benzene, and aqueous alkalis; it does not decolorize permanganate solution or bromine water. With prolonged keeping it gradually darkens.

6. Reaction of Methyl 2-Phenoxyvinyl Ketone with Zinc Chloride. A solution of 15 g of anhydrous zinc chloride in 30 ml of concentrated hydrochloric acid was added to a solution of 15.0 g of methyl 2-phenoxyvinyl ketone in 60 ml of glacial acetic acid. There was no change in outward appearance, and only after two days did the reaction mixture acquire a red color. The solution was filtered, diluted with ether, and treated further as described in the preceding experiment. The product was 1.7 g (29.6%) of 4,4-bis(p-hydroxyphenyl)-2-butanone, m.p. 187° showing no depression in a mixture test with the substance obtained in the preceding experiment.

7. Reaction of Methyl 2-p-Tolyloxyvinyl Ketone with Ferric Chloride. A solution of 10.0 g of ferric chloride in 15 ml of concentrated hydrochloric acid was added to a solution of 5 g of methyl 2-p-tolyloxyvinyl ketone (4-p-tolyloxy-3-buten-2-one) in 30 ml of glacial acetic acid, and the mixture was set aside at room temperature. After one day the crystalline precipitate that had formed was filtered off. Crystallization of glacial acetic acid yielded 5.7 g (56.4%) of violet crystals, m.p. 105°, showing no depression in a mixture test with 2,6-dimethyl-1-benzopyrylium chloroferrate (III) [7].

8. Reaction of 2-Phenoxyvinyl Propyl Ketone with Ferric Chloride. A solution of 15 g of ferric chloride in 22 ml of concentrated hydrochloric acid was added to a solution of 8.0 g of 2-phenoxyvinyl propyl ketone (1-phenoxy-1-hexen-3-one) in 25 ml of glacial acetic acid. The reaction mixture slowly became red, but no precipitate of a pyrylium salt formed. After one day the solution was filtered, diluted with ether, and treated

further as described for Expt. No. 5. Recrystallization of the product from water yielded 1.7 g (28%) of 1,1-bis(p-hydroxyphenyl)-3-hexanone in the form of colorless needles.

Found %: C 76.02; 75.94; H 6.94; 7.09
 $C_{12}H_{20}O_2$. Calculated %: C 76.06; H 7.04

1,1-Bis(p-hydroxyphenyl)-3-hexanone is soluble in ether, benzene, alcohol, and aqueous alkalies; it does not decolorize permanganate solution or bromine water; with keeping it gradually darkens.

9. Preparation of 2-Phenoxyvinyl Phenyl Ketone. To a vigorously stirred solution of 10.0 g of phenol in 60 ml of 15% caustic soda 15.0 g of 2-chlorovinyl phenyl ketone (2-chloroacrylophenone) [7] was added dropwise. The reaction mixture was stirred for twelve hours at room temperature, and the oil that separated was extracted with ether. The extract was washed several times with 10% caustic soda and with water, and then dried over sodium sulfate. The solvent was distilled off, and the residue was vacuum-distilled, the fraction of b.p. 172-183° (4.5 mm) being collected; it crystallized in the receiver. Recrystallization from petroleum ether yielded 8.5 g (42.5%) of 2-phenoxyvinyl phenyl ketone (2-phenoxyacrylophenone) in the form of colorless crystals, m.p. 49-50° (the literature [8] gives 49.5-50°).

Found %: C 80.59; 80.33; H 5.44; 5.37
 $C_{15}H_{12}O_2$. Calculated %: C 80.39; H 5.40

2-Phenoxyvinyl phenyl ketone is of good solubility in the usual organic solvents (poor in petroleum ether). It gradually darkens with keeping.

10. Reaction of 2-Phenoxyvinyl Phenyl Ketone with Ferric Chloride. A solution of 20 g of ferric chloride in 30 ml of concentrated hydrochloric acid was added to a solution of 5.5 g of 2-phenoxyvinyl phenyl ketone in 25 ml of glacial acetic acid. After three hours a crystalline precipitate formed. It was filtered off, washed on the filter with absolute ether, and recrystallized from glacial acetic acid, yielding 0.98 g (10%) of golden scales, m.p. 138°, showing no depression in a mixture test with flavylum chloroferrate (III) [7]. The filtrate from the separation of the flavylum chloroferrate was diluted with ether and repeatedly washed with water until the aqueous layer ceased to be colored. The ether layer was then extracted with 5% caustic soda and the alkaline extract was acidified. Recrystallization of the resulting resinous precipitate from alcohol yielded 0.7 g (20.5%) of colorless crystals, m.p. 198-199°.

Found %: C 79.05; 79.08; H 6.02; 5.91
 $C_{21}H_{14}O_3$. Calculated %: C 79.20; H 5.70

3,3-Bis(p-hydroxyphenyl)propiophenone is soluble in alcohol, ether, boiling water, and aqueous solutions of alkalies.

11. Methylation of 4,4-Bis(p-hydroxyphenyl)-2-butanone. 4,4-Bis(p-hydroxyphenyl)-2-butanone (0.6 g) and methyl iodide (0.8 g) were added to a solution of sodium methoxide prepared by dissolving 1.5 g of sodium in 50 ml of absolute methanol, and the reaction mixture was heated for 30 hours in a water bath. The methanol was distilled off, and 50 ml of 5% caustic soda was added to the residue. The extract was dried over sodium sulfate, and the ether was distilled off. After a few days the residue crystallized out completely. Recrystallization from petroleum ether yielded 0.4 g (60.6%) of colorless needles of 4,4-bis(p-methoxyphenyl)-2-butanone, m.p. 41-42°.

Found %: C 76.00; H 7.01
 $C_{14}H_{20}O_3$. Calculated %: C 76.05; H 7.09

4,4-Bis(p-methoxyphenyl)-2-butanone is of good solubility in the usual organic solvents (poor in petroleum ether).

The semicarbazone was prepared in the usual way. After recrystallization from aqueous alcohol it was obtained as colorless crystals, m.p. 156°.

Found %: N 12.66; 12.73
 $C_{18}H_{22}O_3N_2$. Calculated %: N 12.76

Isolation of 4-(p-hydroxyphenyl)-4-(p-methoxyphenyl)-2-butanone. To the alkaline solution obtained after the extraction of the dimethyl ether of 4,4-bis(p-hydroxyphenyl)-2-butanone, 40 ml of 20% caustic soda was added, when the sodium salt of 4-(p-hydroxyphenyl)-4-(p-methoxyphenyl)-2-butanone, which is sparingly soluble in alkali, separated from the solution. The precipitate was filtered off, dissolved in water, and again precipitated

by addition of alkali. This operation of purification from the dimethyl derivative was repeated four or five times, and the sodium salt of the monomethyl derivative was then dissolved in water and the solution acidified with 20% hydrochloric acid; the crystals that separated were filtered off. Recrystallization from water yielded 0.12 g (19%) of colorless needles, m.p. 121-122°.

Found %: C 75.48; 75.46; H 6.94; 6.77
 $C_{13}H_{14}O_2$. Calculated %: C 75.53; H 6.71

The needles dissolve readily in ether and alcohol; less readily in hot water.

When 4,4-bis(p-hydroxyphenyl)-2-butanone was methylated under the usual conditions with dimethyl sulfate, the dimethyl derivative was obtained in 65.2% yield, and the monomethyl derivative in 17% yield.

12. Oxidation of 4,4-Bis(p-methoxyphenyl)-2-butanone. To a suspension of 1.5 g of the substance in 50 ml of a 5% solution of sodium carbonate, 4.4 g of finely ground potassium permanganate was added, and the reaction mixture was boiled for three hours. The mixture was cooled, and the precipitate of manganese dioxide and 4,4'-dimethoxybenzophenone was filtered off and washed carefully on the filter, first with 10% sodium carbonate solution, and then with a saturated solution of oxalic acid. The undissolved residue was recrystallized from alcohol, and yielded colorless crystals, m.p. 142-143°, showing no depression in a mixture test with 4,4'-dimethoxybenzophenone.

13. Reaction of 4-(p-Methoxyphenyl)-3-buten-2-one with Phenol. Phenol (0.5 g) and a solution of 4.0 g of anhydrous zinc chloride in 5 ml of concentrated hydrochloric acid were added to a solution of 0.7 g of 4-(p-methoxyphenyl)-3-buten-2-one in 20 ml of glacial acetic acid, and the reaction mixture was set aside for two days at room temperature. The mixture was then diluted with 150 ml of ether and washed with water until the washings ceased to be colored. The ether layer was extracted with a 3% solution of caustic soda, and the alkaline extract was acidified with 20% hydrochloric acid. The precipitated crystals of 4-(p-hydroxyphenyl)-4-(p-methoxyphenyl)-2-butanone (0.7 g, i.e. 69%) were filtered off. Recrystallization from water yielded colorless crystals, m.p. 121-122°, showing no depression in a mixture test with the substance obtained in Expt. No. 11.

SUMMARY

1. It has been shown that in the reaction of 2-phenoxy- and 2-(2-naphthoxy)-vinyl ketones with ferric chloride in a mixture of acetic and concentrated hydrochloric acids, a rearrangement associated with the migration of the 3-oxo-1-alkenyl group to the ortho- and para-positions in the aromatic nucleus takes place.
2. 2-(2-Naphthoxy)- and 2-phenoxy-vinyl ketones having a para-substituent in the aromatic nucleus give α -substituted naphtho- and benzo-pyrylium salts when treated with ferric chloride.
3. 2-Phenoxyvinyl ketones having no para-substituent in the aromatic nucleus give mixtures of the benzo-pyrylium salt and the alkyl 2,2-bis(p-hydroxyphenyl)ethyl ketone when treated with ferric chloride.
4. It has been shown that zinc chloride in hydrochloric acid also promotes the rearrangement of phenoxy-vinyl ketones, resulting in the formation of only alkyl 2,2-bis(p-hydroxyphenyl)ethyl ketones.
5. It has been shown that, in presence of zinc chloride, 4-(p-methoxyphenyl)-3-buten-2-one unites at its double bond with a molecule of phenol.

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* See Consultants Bureau Translation, page 429.

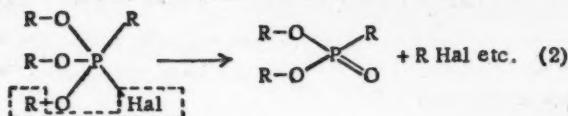
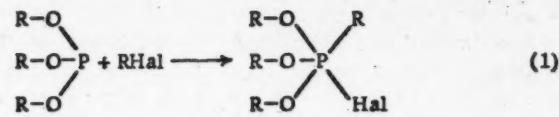
EFFECT OF THE SIZE AND STRUCTURE OF RADICALS PRESENT
IN PHOSPHORUS ESTERS ON THE RATE OF ISOMERIZATION
OF THESE SUBSTANCES*

A. E. Arbuzov and L. V. Nesterov

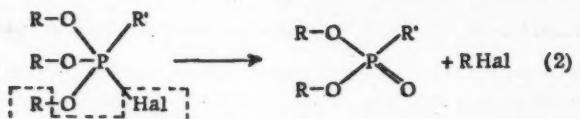
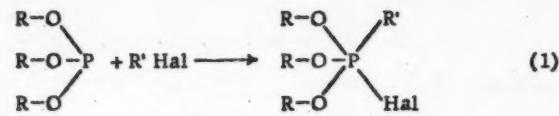
In 1905, while studying the reaction of trialkyl phosphites with alkyl halides, one of us [1] discovered the isomerization of trialkyl phosphites into esters of alkylphosphonic acids. Further study of this reaction showed that it is catalytic, since the amount of alkyl halide can be reduced to a very low value without affecting the yield. Such is the process that occurs when the alkyl of the alkyl halide is identical with the alkyls of the phosphorous ester.

When the trialkyl phosphite was treated with an equimolecular amount of an alkyl halide in which the alkyl was not identical with the alkyls of the phosphorous ester, a reaction was found to occur which has since been given the name of the "Arbuzov rearrangement". At the same time a mechanism was proposed for these transformations: the isomerization and rearrangement reactions proceed in two stages. The first stage consists in the addition of alkyl halide to trialkyl phosphite. In the case of the isomerization reaction the addition product is extremely unstable, and the second stage, elimination of alkyl halide in which an ester alkyl is removed, sets in at the same temperature. When the trialkyl phosphite is treated with an alkyl halide containing an alkyl of different molecular weight or structure, then, as in the case of isomerization, in the first stage an addition product is formed, and in the second stage there occurs the elimination of the halide of the alkyl originally present in the trialkyl phosphite. All of these reactions are shown in the schemes below:

Isomerization of phosphorous esters:

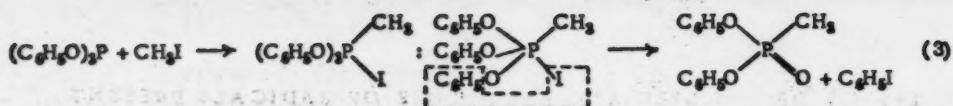


"Arbuzov rearrangement":



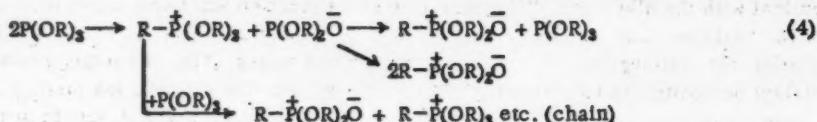
In the case of phosphorous esters in which R is an aliphatic radical, it has not been found possible to isolate, or even to detect, the intermediate addition product, but in the case of esters in which R is aromatic, the addition product is sometimes stable and may be isolated in the analytically pure state. These addition products are crystalline products, and they were first obtained by chemists of the Michaelis school [2]. With the aid of one of these, the product of the addition of methyl iodide to triphenyl phosphite, direct confirmation was obtained of the above scheme for the mechanism of the rearrangement. In this case the two stages can be effected separately:

• A study of the mechanism of the Arbuzov rearrangement.



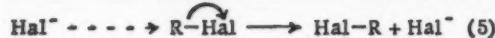
The addition (the first stage) goes at 100°, and the decomposition (the second stage) at a much higher temperature. This is the only case that has been described of the separate realization of the two stages of the Arbuzov rearrangement. An attempt to decompose the analogous addition products formed by methyl iodide with the phenyl esters of phenylphosphonous and diphenylphosphinous acids [3] was not successful.

In spite of the fact that in many cases it has not been found possible to isolate the intermediate addition products, there can be little doubt that they are formed. This scheme has been confirmed by all of the great variety of syntheses (more than 300) carried out by Soviet and foreign chemists. By means of the Arbuzov rearrangement, compounds have been obtained containing the linkages phosphorus-carbon, phosphorus-silicon, phosphorus-tin, phosphorus-phosphorus, and phosphorus-arsenic. The above scheme of the mechanism of the Arbuzov rearrangement in its general form is accepted by the majority of chemists. Only Rumpf [4] regards the rearrangement (more accurately, its special case: isomerization) as a chain reaction, for which he proposes the following scheme:



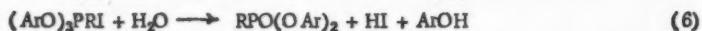
Rumpf, however, gives no experimental confirmation of his scheme, but refers to the possibility of obtaining derivatives of methylphosphonic acid by heating pure dimethyl phosphite.

Although the general scheme of the rearrangement reaction is almost universally accepted, views on particular details are at variance. The first stage, i.e., addition, is regarded by all authors as analogous to the well-known Menshutkin reaction [5], which, according to Menshutkin's own investigations, is a second-order reaction. The intermediate addition product is regarded as a phosphonium derivative $[(RO_2PR')_2]^+Hal^-$. Gerrard and Green [6] bring forward experimental proof of the formation of halide ions in the reaction medium during the reaction of trialkyl phosphites with alkyl halides. Optically active 1-methylheptyl halide present in such a mixture, is gradually racemized, which the authors explain by the following scheme of ion exchange:



and they consider that the racemization proves the presence of halide ions. The reaction was carried out at about 100°. The authors, however, do not describe any blank experiment on the racemization of 1-methylheptyl halide under the same temperature conditions.

The crystalline addition products are of low stability [1, 2, 3], and react with water [2] according to the equation:

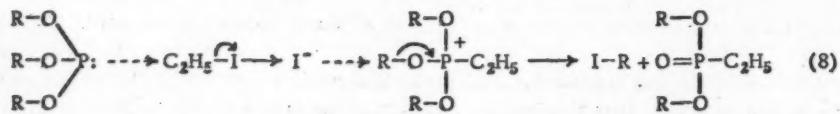


and with alcohols [1, 3] according to the equation:



Incidentally, the last reaction has been proposed as a general method for the preparation of the alkyl halides $R'Cl$.

As regards the second stage of the reaction, different authors treat it in different ways. Gerrard and Green [6] consider that the second stage is a bimolecular reaction proceeding according to the scheme:



If R is the radical of an optically active alcohol, then after the reaction the radical of the alkyl halide IR acquires the reverse configuration, thus confirming the bimolecular mechanism of the reaction.

- The British authors Landauer and Rydon ascribe the priority of the discovery of the reaction in Equation 7 to themselves, although it was described by one of us [1] 45 years previously.

Pudovik [7] supposes that the second stage is bimolecular only when the radical R of the phosphorous ester $P(OR)_3$ is primary. When the radical is secondary, the reaction may be either uni- or bi-molecular, and when it is tertiary, the reaction may be only unimolecular. For primary radicals, therefore, Pudovik proposes a scheme completely analogous to Gerrard's scheme. In the case of secondary radicals, first of all an unsaturated carbonium ion is eliminated (by a unimolecular mechanism), and in this oscillation of the double bond occurs, so that when it unites with a halide ion a mixture of almost equal amounts of isomeric alkyl halides is obtained. All these conclusions, however, are based on indirect evidence; no observations have been made of the kinetics of the second stage of the rearrangement of aliphatic phosphorous esters, and it does not appear to be possible to carry out such observations.

Observations on the kinetics of the Arbuzov rearrangement have been made [8, 9, 10] only in a few special cases of isomerization. Observations on the general case of rearrangement have been made only once [11], and these cannot pretend to high accuracy. The first investigations of this sort were carried out in 1914 [8]. It was established that the isomerization was not a first-order reaction, but was similar to catalytic (enzymic) processes. The isomerization curves had a characteristic S bend, i.e., in the first stages of the reaction it was accelerated, as if proceeding contrary to the mass-action law. The effect of self-heating on the process was excluded by careful thermodynamic control. The question of the autocatalytic effect of the isomerization product was answered in the negative [8], since a mixture of the pure phosphorous ester and its isomer underwent no change when heated for a long time at 155°.

Zawidski and Staronka [9], however, gave a different answer to the question of the autocatalytic effect of the isomerization product. They supposed that the isomerization product speeds up the reaction, but only in presence of alkyl halide. They considered, therefore, that in the case of isomerization "complex" autocatalysis is observed; for the rate of such a reaction they proposed the equation:

$$\frac{dx}{dt} = k(1+nx)(1-x). \quad (9)$$

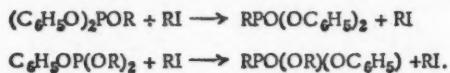
(x is the relative concentration of the reaction product, and n is a constant in a given experiment). When the reaction is carried out in a solvent, the "conjugation" between the alkyl halide and the isomerization product is broken, and the accelerating effect of the latter does not appear. Staronka [10] has proposed another interpretation for Equation 9, the basis of this being the variation of the composition of the medium in which the reaction occurs.

In the present investigation we have carried out isomerization experiments on some new mixed phosphorous esters, experiments on the addition of alkyl iodides to triphenyl phosphite, and experiments on the thermal decomposition of the addition products; the rates of all of these reactions have been studied.

EXPERIMENTAL

Preparation of Mixed Phosphorous Esters, and their Isomerization. Mixed aliphatic-aromatic phosphorous esters were studied: they were prepared from phenyl phosphorodichloridite and diphenyl phosphorochloridite and the corresponding alcohols in an ether medium by Milobendzsky's method. Dimethylaniline and, in one case, pyridine were used as agents for binding hydrogen chloride. Altogether, seven mixed phosphorous esters were synthesized. They are all colorless, fairly mobile liquids, which react with cuprous halides with evolution of heat. A crystalline cuprous chloride addition product, m.p. 69°, was prepared from methyl diphenyl phosphite; it was not found possible to crystallize the other addition products. The properties of the mixed phosphorous esters are given in Table 1 (Nos. 1-7).

The reactions of all of these phosphorous esters with the corresponding alkyl iodide were studied. The reactions were carried out in sealed tubes, and equimolecular amounts of the reagents were taken. Smooth isomerization occurred only in the case of dimethyl phenyl, methyl diphenyl, diethyl phenyl, and ethyl diphenyl phosphites, and the reactions then went according to the equations:



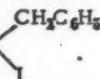
The properties of the resulting phenyl and mixed esters of alkylphosphonic acids are given in Table 1 (Nos. 8-11). All of these esters are liquids of higher viscosity than the isomeric phosphorous esters. Product No. 8 is soluble in water in all proportions; the remainder are not appreciably soluble in water.

The phosphorous esters Nos. 3, 4, and 5 do not appear to react with the corresponding alkyl iodides below 200°; above 200° decomposition sets in. We, therefore, prepared the phenyl esters of the higher alkylphosphonic acids by another method.

TABLE 1

No.	Ester	Temperature (°C) (p in mm Hg)	d_0^{25}	n_D^{25}	MR		Yield (%)
					found	calc'd	
1	$(C_6H_5O)_2POCH_3$	165.5 - 166.5 (12)	1.1644	1.5528	68.18	68.10	56
2	$(C_6H_5O)_2POC_2H_5$	182 - 183 (17.5)	1.1372	1.5475	73.18	72.72	60.5
3	$(C_6H_5O)_2PO 1-C_3H_7$	170 - 171 (10)	1.1073	1.5394	78.20	77.33	58
4	$(C_6H_5O)_2PO p-C_4H_9$	187 - 187.5 (9.5)	1.0967	1.5370	82.66	81.95	52
5	$(C_6H_5O)_2PO 1-C_4H_9$	180.5 - 181 (9)	1.0952	1.5358	82.62	81.95	68
6	$C_6H_5OP(OCH_3)_2$	96 - 97 (9)	1.1267	1.5053	49.03	48.61	50.6
7	$C_6H_5OP(OC_2H_5)_2$	113 (11)	1.0659	1.4933	58.44	57.85	35.3
8	$CH_3PO(OCH_3)(OC_6H_5)$	135 - 136 (11)	1.1914	1.5054	46.37	46.41	98.5
9	$C_2H_5PO(OC_2H_5)(OC_6H_5)$	142.5 - 143.5 (12.5)	1.1197	1.4922	55.52	55.65	84
10	$CH_3PO(OC_6H_5)_2$	192 - 192.5 (9)	1.2058	1.5518	65.75	65.90	88.3
11	$C_2H_5PO(OC_6H_5)_2$	202 (13)	1.1799	1.5451	70.29	70.52	80
12	$1-C_3H_7PO(OC_6H_5)_2$	198 - 200 (10.5)	1.1497	1.5383	75.20	75.14	33.7
13	$p-C_4H_9PO(OC_6H_5)_2$	205 - 207.5 (11)	1.1293	1.5339	79.89	79.76	52
14	$1-C_4H_9PO(OC_6H_5)_2$	190 - 192 (11.5)		M.p. 66°			35
15	$C_6H_5CH_2PO(OC_6H_5)_2$			M.p. 104°			76

TABLE 2

No.	Substance	Temperature (°C)		Amount of I (%)		Yield (%)
		of prep.	of melting	found	calc'd	
16	$(C_6H_5O)_3P$ 	120	112-114	24.23	24.02	Quantitative
17	$(C_6H_5O)_3P$ 	130	130	28.31; 28.32	28.06	Quantitative
18	$(C_6H_5O)_3P$ 	130	89-91	27.43; 27.31	27.16	Quantitative
19	$(C_6H_5O)_3P$ 	160	110	26.58; 26.57	26.43	12.1
20	$(C_6H_5O)_3P$ 	170		Not isolated in pure state		
21	$(C_6H_5O)_3P$ 	150	157-157.5	26.61; 26.67; 26.87	25.68	

Preparation of the Addition Products of Alkyl Iodides with Triphenyl Phosphite. The addition products of alkyl iodides with triphenyl phosphite were prepared by Michaelis' method. An equimolecular mixture of triphenyl phosphite and alkyl iodide was sealed in a tube, which was then heated at a definite temperature (Table 2: temperature of preparation) until the reduction in volume stopped. With one exception, all of the addition products were obtained in the crystalline state and were recrystallized from a mixture of dichloroethane and ether; their properties are given in Table 2.

It was not found possible to purify the isobutyl iodide addition product (No. 21) sufficiently to obtain satisfactory analytical figures, although the product was purified by means of four careful recrystallizations, and the melting point of the crystals did not change in the last two of these. We did not succeed in elucidating the cause of the nonagreement of the analyses.

Reaction of Alkyltriphenoxyphosphonium Iodides with Alcohol. The phenyl esters of higher alkylphosphonic acids, which we were unable to prepare by isomerization of the corresponding mixed phosphorous esters, were prepared by the reaction of Equation 7. The properties of the resulting esters are given in Table 1 (Nos. 12-15).

Thermal Decomposition of Alkyltriphenoxyphosphonium Iodides. All of the alkyltriphenoxyphosphonium iodides that we prepared were subjected to heating in sealed tubes at 210-220°. Decomposition then occurred in accordance with the scheme for the second stage of the Arbuzov rearrangement. Decomposition was accompanied by resinification processes, particularly in the case of the higher homologs. An appreciable amount of iodine separated, and this greatly complicated the purification process. We removed iodine by a new method, namely, by means of trimethyl phosphite. The results of the experiments are given in Table 3.

TABLE 3

Substance	Decomposition temperature, °C (time in hours)	Yield (%)		B.p. of $\text{RPO}(\text{OPh})_2$ in °C (p in mm Hg)		n_{D}^{20} of pure substance	n_{D}^{20} of sub. obtained
		$\text{C}_6\text{H}_5\text{I}$	$\text{RPO}(\text{OPh})_2$	of pure sub.	of sub. obtained		
$(\text{C}_6\text{H}_5\text{O})_3\text{P}(\text{CH}_3)\text{I}$	220 (20)	74	56	192-192.5 (9)	196-199 (12)	1.5518	1.5520
$(\text{C}_6\text{H}_5\text{O})_3\text{P}(\text{C}_2\text{H}_5)\text{I}$	220 (20)	71	60	202 (13)	200-204 (12)	1.5451	1.5454
$(\text{C}_6\text{H}_5\text{O})_3\text{P}(\text{i-C}_3\text{H}_7)\text{I}$	208 (15)	35	(50)	198-200 (10.5)	202-205 (12)	1.5383	1.5480
$(\text{C}_6\text{H}_5\text{O})_3\text{P}(\text{n-C}_4\text{H}_9)\text{I}$	220 (15)	15	(51)	205-207.5 (11)	203-209 (10)	1.5339	1.5410
$(\text{C}_6\text{H}_5\text{O})_3\text{P}(\text{CH}_2\text{C}_6\text{H}_5)\text{I}$	208 (20)	15	--	--	--	--	--
$(\text{C}_6\text{H}_5\text{O})_3\text{P}(\text{i-C}_4\text{H}_9)\text{I}$	210 (15)			Only crystalline iodine isolated			

In the decomposition products of n-butyltriphenoxyphosphonium iodide, it was shown that not less than 75% of diphenyl n-butylphosphonate was present (isolated as crystalline n-butylphosphonic acid from the hydrolyzed high-boiling fraction). In the decomposition products of isopropyltriphenoxyphosphonium iodide, only iodobenzene was detected. The high-boiling fraction probably contained diphenyl isopropylphosphonate, but we did not succeed in isolating isopropylphosphonic acid from the hydrolysis products.

The formation and decomposition of alkyltriphenoxyphosphonium iodides provide confirmation of the scheme of the Arbuzov rearrangement proposed by its discoverer.

Study of the Kinetics of the Reaction. The procedure employed in the observations on the kinetics of the isomerization was based on the change in the volume of the reaction mixture and has been described in great detail by A. E. Arbuzov [8]. No essential modifications were introduced in our experiments. Equimolecular proportions of reactants were taken in the reaction mixtures. Each phosphorous ester isomerization reaction and reaction of addition of alkyl iodide to triphenyl phosphite was studied at two different temperatures. From the figures obtained the temperature coefficients of the reactions were calculated, and the results for all of the reactions were reduced to the same temperature.

Table 4 gives the main results of the isomerization experiments and Table 5 gives the results of the addition experiments.

TABLE 4

Original mixture	Temp. of expt. (°C)	Time (min) for a conversion of				Temp. coeff.	Time for 100% conversion adjusted to 100°(hours)
		25%	50%	75%	100%		
$(C_6H_5O)_2POCH_3 + CH_3I$	80.3	108	200	315	790	1.94	3.6
	92	49	92	146	345		
$(C_6H_5O)_2POC_2H_5 + C_2H_5I$	110	6.25 hour	13.25	21.67	60	1.96	117.5
	156		16.5	35	62.5		
$C_6H_5OP(OCH_3)_2 + CH_3I$	64.5	48	86	130	315	2.34	0.41
	72	28	45	64	180		
$C_6H_5OP(OC_2H_5)_2 + C_2H_5I$	110	66	133	222	507	2.10	17.7
	130	14	30	55	195		

TABLE 5

RI	Temp. of expt. (°C)	Time (hr) for addition of				Temp. coeff.	Time for 100% addition adjusted to 100°(hours)
		25%	50%	75%	100%		
$C_6H_5CH_2I$	110	0.484	0.833	1.25	3.75	1.88	8.52
	130	0.14	0.23	0.35	1.65		
CH_3I	110	0.63	1.33	2.53	10.75	1.97	19.4
	130	0.17	0.33	0.64	2.50		
C_2H_5I	110	18.0	38.5	70.0	—	2.10	510
	155	0.724	1.326	2.20	8.50		
$1-C_3H_7I$	176	3.75	7.1	10.35	21.0	(2)	4200
$n-C_4H_9I$	155	2.85	5.38	12.17	36.0	2.05	2120
	176	0.55	1.25	2.94	10.0		
$1-C_4H_9$	155	4.71	5.22	5.94	7.00	1.83	214
	176	1.26	1.52	1.69	2.33		

The isomerization curves that we obtained did not correspond to a reaction of the first order; neither could they be described by Equation 9 of Zawidzki and Staronka. Since the addition of alkyl iodides to triphenyl phosphite is accompanied by various side reactions and resinifications, particularly in the case of the higher homologs, the reaction curves cannot, of course, characterize the processes correctly. However, in the majority of cases they were fairly close to first-order reaction curves.

The addition of isobutyl iodide to triphenyl phosphite calls for special comment, for it is about ten times as rapid as the addition of *n*-butyl iodide, and at the same time it has a considerable induction period. We intend to study this case in greater detail. The decomposition of alkyltriphenoxyphosphonium iodides was accompanied by increase in volume, which permitted us to follow the kinetics of the reactions by the same method as that used in the preceding experiments. The temperature of the experiments was 208°. The results are given in Table 6.

In order to determine the effect of the reaction product on the rate of isomerization, we carried out a number of experiments on the isomerization of dimethyl phenyl phosphite, and in these we added various amounts of methyl phenyl methylphosphonate to the original equimolecular mixture of methyl iodide and the phosphorous ester at the beginning of the experiment. All of the experiments were carried out at 64.5°. The composition of

of the original mixture was $C_6H_5OP(OCH_3)_2 + xCH_3PO(OCH_3)(OC_6H_5) + CH_3I$. The results are given in Table 7.

TABLE 6

Substance	Time (hr) for decomposition of			
	25%	50%	75%	100%
$(C_6H_5O)_3P-CH_2C_6H_5$	0.4	1.38	4.18	18.0
$(C_6H_5O)_3P-CH_3$	3.2	7.8	15.6	30
$(C_6H_5O)_3P-C_2H_5$	3.7	8.2	14.0	32
$(C_6H_5O)_3P-1-C_3H_7$	2.4	5.1	9.5	19
$(C_6H_5O)_3P-n-C_4H_9$	2.42	4.5	8.67	17.5

TABLE 7

x	Time (min) in which the percentage of the phosphorous ester that reacted was			
	25%	50%	75%	100%
0.000	48	86	130	315
0.200	39	71	110	240
0.500	34	67	107	230
1.000	32	62	105	240

Addition of the isomer to the original mixture, it will be seen, accelerates the reaction. The gradual acceleration of the reaction observed by various authors and by us is to be explained by the autocatalytic effect of the reaction product, which apparently acts as a solvent in which the rate of isomerization is appreciably greater than in the original mixture.

SUMMARY

1. Some new dialkyl phenyl and alkyl diphenyl phosphites have been synthesized.
2. In the series of alkyl diphenyl phosphites, only the methyl and ethyl esters isomerize smoothly. The higher homologs decompose when they react with the corresponding alkyl iodides.
3. A number of new addition products of alkyl iodides with triphenyl phosphite has been prepared.
4. The products of the addition of methyl, ethyl, and n-butyl iodides to triphenyl phosphite decompose at 210-220° according to the scheme of the second stage of the Arbuzov rearrangement.
5. By the action of alcohol on the products of the addition of benzyl, isopropyl, n-butyl, and isobutyl iodides to triphenyl phosphite, the diphenyl esters of the corresponding alkylphosphonic acids have been prepared; these reactions confirm the structures of the addition products.
6. The above facts (3, 4, and 5) show that the Arbuzov rearrangement occurs in two stages with the formation of an intermediate addition product.
7. It has been shown that the isomerization products of phosphorous esters are substances that accelerate the isomerization process. The isomerization reaction is therefore autocatalytic.
8. Isobutyl iodide adds to triphenyl phosphite considerably more rapidly than n-butyl iodide does. The addition reaction of isobutyl iodide, unlike those of the other alkyl iodides examined, has a long induction period.

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with a fairly large atomic refractivity due to atoms which are not bound but which are attached to one another in such a way that the reaction occurs. In some cases starting from a group of molecules we can find the atomic refractivity of each atom in the molecule. For example, the atomic refractivity of the atoms in the molecule $\text{C}_2\text{H}_5\text{CH}_2\text{CH}_2\text{O}_2\text{C}_2\text{H}_5$ is 1.510, and the atomic refractivity of the atoms in the molecule $\text{C}_2\text{H}_5\text{CH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{O}_2\text{C}_2\text{H}_5$ is 1.511.

ATOMIC REFRACTION OF PHOSPHORUS AND SULFUR IN PHOSPHOROTHIOL THIONIC ESTERS

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As is well known, the value of the atomic refraction of phosphorus in organic compounds is highly subject to constitutive effects: it depends on the valency state of the element and on the character of the bonds that it forms. Investigations on the atomic refraction of phosphorus have been carried out by Kovalevsky [1], Arbuzov [2], Jones, Davies, and Dyke [3], and others. In 1948 one of us [4] worked out the most probable values of the atomic refraction of phosphorus in certain types of organophosphorus compounds. Thus, for trialkyl phosphites the value determined (D line of sodium) was 7.04, for alkyl esters and other derivatives of phosphoric, phosphorochloridic, and phosphorodichloridic acids it was 3.76, and for derivatives of alkylphosphonic acids (esters and acid chlorides) it was 4.27. In the derivation of these constants, the generally accepted atomic refraction constants of Eisenlohr were used, the value assumed for chlorine attached to phosphorus being that found for chlorine in acid chlorides, namely 6.336 [5]; for the oxygen of the $\text{P}=\text{O}$ group the value 2.211 was taken. The values so derived for the atomic refraction of phosphorus have been used since by many investigators [6], who have obtained good agreement between found and calculated values of the molecular refractions of organophosphorus compounds.

In the case of molecular refraction calculations on organic compounds containing sulfur and phosphorus, there is, as yet, an absence of reliable data on the atomic refraction of sulfur attached to phosphorus in the various types of these compounds. Jones, Davies, and Dyke [3] calculated the atomic refractions of sulfur in trimethyl phosphorothionate and trimethyl phosphorothiolate, and obtained the values 6.23 and 7.49 respectively. These values were calculated by the use of atomic constants for carbon, hydrogen, and oxygen that differed from Eisenlohr's constants, and the value 9.14 was used for the atomic refraction of phosphorus. Suitable recalculation of the results yields the values 9.68 for the sulfur of the $\text{P}=\text{S}$ group and 8.12 for the sulfur of the $\text{P}-\text{S}-\text{R}$ group. Although the first of these values has been confirmed by later results [7], the value of the atomic refraction of thiol sulfur in organophosphorus compounds continues to rest on the single example mentioned.

Molecular refraction calculations for organophosphorus compounds show that, when the above-cited atomic constants are used for phosphorus, the values of the atomic refractions of carbon, hydrogen, oxygen, and the halogens, and of the constitutive increments, remain the same as those established for the corresponding carbon compounds [4]. It is, therefore, of interest to determine whether the values of the atomic refraction of sulfur attached to phosphorus correspond to those of sulfur attached to carbon.

The atomic refraction of sulfur in carbon compounds has been the subject of numerous investigations. In a long paper by Boudet and Rambaud [8] there is a review of the available data on this question, and, on the basis of numerous examples, the values of the atomic refraction of sulfur (D line of sodium) are determined for various sulfur compounds. In particular, for the doubly bound sulfur of thiones the value 9.70 is obtained; in alkanethiols sulfur has the value 7.81, in dialkyl sulfides 8.00, and in alkyl aryl sulfide 9.20. The group S_2 in alkylxanthic

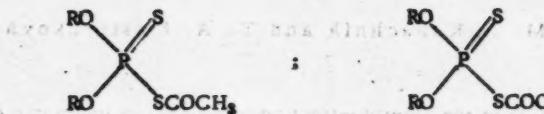
esters $\text{RO}-\text{C}(=\text{S})-\text{SR}'$ and alkanecarbodithioic esters $\text{R}-\text{C}(=\text{S})-\text{SR}'$ is characterized, according to their results, by an

average group refraction of 18.78. According to Vogel [9], the refraction of sulfur in dialkyl sulfides is 7.92. In the case of alkylxanthic esters he uses a method of calculating group refractions that differs from that generally accepted. When the group refraction of S_2 is calculated in the usual way from his experimental results, the value obtained is 18.67, which is in good agreement with Boudet and Rambaud's results.

Having synthesized for the first time pure O,O -dialkyl S -hydrogen phosphorothiolothionates $(\text{RO})_2\text{PSSH}$ [10], which are phosphorus analogs of xanthic acids, we determined the group refraction of the two sulfur atoms in these compounds*. It was found to be 18.82 ± 0.07 , i.e., almost equal to the value 18.78 derived by

* There is a misprint in the paper cited [10] on page 729: The value of the atomic refraction of thiol sulfur is given at 9.34, instead of 9.06.

Boudet and Rambaud for the two sulfur atoms of the alkylxanthic esters and alkanecarbodithioic esters. With a view to making a more complete comparison of the atomic refractions of sulfur in derivatives of phosphorothiolothionic and alkylxanthic acids, we have synthesized, apart from the above-mentioned O,O-dialkyl S-hydrogen phosphorothiolothionates, some trialkyl phosphorothiolothionates (RO₃PS(SR) and some S-acyl derivatives of O,O-dialkyl S-hydrogen phosphorothiolothionates of two types (which will be named in this paper as O,O-dialkyl S-acyl (or S-alkoxycarbonyl) phosphorothiolothionates):

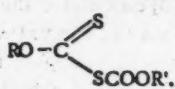


The results obtained are given in the table.

It was found that the average value of the group refraction of S₂ is 18.72 ± 0.07 in the trialkyl phosphorothiolothionates, and 19.77 ± 0.03 in the acyl derivatives.

As will be seen from the table, among compounds of a given type the refraction of the group S₂ retains a constant value, the departure from the mean value being small and not outside the usual errors of measurement. A comparison of the refractions of the group S₂ in trialkyl phosphorothiolothionates and alkylxanthic esters (18.72 and 18.78) shows that the group S₂ has the same refraction in combination with phosphorus and in combination with carbon. This again confirms the hypothesis referred to above concerning the equality of the atomic refractions of elements in combination with carbon and with phosphorus.

The S-acyl derivatives of O,O-dialkyl S-hydrogen phosphorothiolothionates are characterized by a higher value of the group refraction of the two sulfur atoms, namely 19.77. This value should be compared with the refraction of sulfur in the corresponding acyl derivatives of alkylxanthic acids:

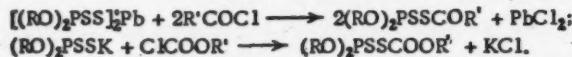


Substances of this type are known. Thus, the ethyl derivative has d₄²⁰ 1.180 and n_D²⁰ 1.527 [11]. From these figures the refraction of the two sulfur atoms is found to be AR_{S₂} 19.53, which is near to the value 19.77, which we obtained for S-acyl derivatives of O,O-dialkyl S-hydrogen phosphorothiolothionates.

No.	Compound	B.p. in °C (p in mm Hg)	n _D ²⁰	d ₄ ²⁰	Found MR _D	AR _{S₂}	Mean value of AR _{S₂}
1	(CH ₃ O) ₂ PSSH	62-68 (4.5)	1.5343	1.2888	38.16	18.58	
2	(C ₂ H ₅ O) ₂ PSSH	81.5-82.5 (5)	1.5070	1.1654	47.56	18.74	
3	(C ₃ H ₇ O) ₂ PSSH	85-86 (3)	1.4987	1.1040	56.96	18.91	18.82 ± 0.07
4	(i-C ₃ H ₇ O) ₂ PSSH	71-72 (3)	1.4918	1.0911	56.96	18.91	
5	(i-C ₄ H ₉ O) ₂ PSSH	93 (4)	1.4889	1.0558	66.23	18.94	
6	(CH ₃ O) ₂ PS(SCH ₃)	101-101.5 (16.5)	1.5292	1.2415	42.79	18.59	
7	(C ₂ H ₅ O) ₂ PS(SC ₂ H ₅)	115-115.5 (10)	1.5013	1.1168	56.56	18.50	
8	(C ₃ H ₇ O) ₂ PS(SC ₃ H ₇)	115-116 (3)	1.4955	1.0561	70.85	18.94	18.72 ± 0.07
9	(i-C ₃ H ₇ O) ₂ PS(SC ₃ H ₇ -i)	91-92 (3)	1.4843	1.0351	70.90	18.99	
10	(i-C ₄ H ₉ O) ₂ PS(SC ₄ H ₉ -i)	148-149 (4)	1.4859	1.0159	84.33	18.57	
11	(C ₂ H ₅ O) ₂ PS(SCOOCH ₃)	98 (2)	1.5154	1.1898	57.89	19.82	
12	(i-C ₃ H ₇ O) ₂ PS(SCOOCH ₃)	100-101 (3)	1.4979	1.1177	67.21	19.90	
13	(i-C ₄ H ₉ O) ₂ PS(SCOOCH ₃)	125-126 (3)	1.4929	1.0793	76.56	19.71	
14	(C ₂ H ₅ O) ₂ PSSCOOCH ₃)	105-106 (3.5)	1.5063	1.2171	59.66	19.95	
15	(C ₂ H ₅ O) ₂ PS(SCOOOC ₂ H ₅)	115 (4)	1.5001	1.1891	63.90	19.57	19.77 ± 0.03
16	(C ₂ H ₅ O) ₂ PS(SCOOOC ₃ H ₇)	125 (5.5)	1.4981	1.1620	68.70	19.75	
17	(C ₂ H ₅ O) ₂ PS(SCOOOC ₄ H ₉ -i)	162-163 (6)	1.4889	1.1281	73.25	19.68	
18	(C ₂ H ₅ O) ₂ PS(SCOOOC ₅ H ₁₁ -i)	137-138 (4)	1.4925	1.1179	78.04	19.85	
19	(i-C ₃ H ₇ O) ₂ PS(SCOOOC ₂ H ₅)	109-109.5 (3)	1.4894	1.1301	73.18	19.61	
20	(i-C ₃ H ₇ O) ₂ PS(SCOOOC ₅ H ₁₁ -i)	137-138 (3)	1.4841	1.0773	87.24	19.82	

As mentioned above, the value of the atomic refraction of sulfur bound to phosphorus in the P=S group of trimethyl phosphorothionate is 9.68, i.e., very close to the atomic refraction of thione sulfur, 9.70. If we assume that this value is preserved also in the O,O-dialkyl S-hydrogen phosphorothiolothionates, we may calculate the atomic refractions of thiol sulfur in the groups P-S-H and P-S-R and of thioanhydride sulfur in the group P-S-CO-, the values obtained are 9.12, 9.02, and 10.07 respectively. The second of these values should be compared with the value of 8.12 found by Jones, Davies, and Dyke for trimethyl phosphorothiolate. Whether this lack of agreement ($\Delta = 0.90$) is due to constitutive effects, or to inadequate accuracy in the determination of the refraction of thiol sulfur, which was based by these authors on a single observation, it is, as yet, impossible to say.

We have already [10] described the syntheses of O,O-dialkyl S-hydrogen phosphorothiolothionates and trialkyl phosphorothiolothionates. O,O-Dialkyl S-hydrogen phosphorothiolothionates have been prepared also by Malatesta and Laverone [2]. The S-acyl derivatives of O,O-dialkyl S-hydrogen phosphorothiolothionates were prepared by us in high yields from the corresponding sodium, potassium, or lead salts and acyl halides, for example:



The acetyl derivatives were obtained equally readily from the potassium, sodium, and lead salts. The benzoyl derivative examined could be obtained only from the lead salt; on the other hand, the alkoxy carbonyl derivatives could be obtained only from the alkali-metal salts.

EXPERIMENTAL

O,O-Diethyl S-Acetyl Phosphorothiolothionate was prepared: 1. From Lead Bis[O,O-diethyl phosphorothiolothionate]. Acetyl chloride (7.8 g, i.e. 0.1 mole) was added to 11.5 g (0.02 mole) of lead bis[O,O-diethyl phosphorothiolothionate]. The mixture became warm, and the bulk of the solid present became less. The reaction mixture was heated at 65-80° in a water bath for two hours under reflux. When the mixture was cool, the lead chloride was filtered off and washed with benzene; 5.2 g was obtained (theoretical amount 5.56 g). The filtrate was dried over sodium sulfate and vacuum-fractionated. Two distillations yielded 7.8 g (85%) of a substance of b.p. 98° (2 mm).

O,O-Diethyl S-acetyl phosphorothiolothionate was obtained as an orange liquid; n_D^{20} 1.5154; d_4^{20} 1.1898; found MR 57.89; calculated MR 57.84.

Found %: C 31.55; 31.54; H 5.78; 5.85; P 13.63; 13.60
 $C_8H_{12}O_3PS_2$. Calculated %: C 31.58; H 5.70; P 13.60

2. From Potassium O,O-Diethyl Phosphorothiolothionate. Acetyl chloride (11.78 g, i.e. 0.15 mole) was added to 10.12 g (0.05 mole) of potassium O,O-diethyl phosphorothiolothionate. The mixture immediately became warm. The solid present changed from the crystalline (scales) to the amorphous state. The reaction mixture was heated in a water bath at 65-70° for two hours under reflux. When the mixture was cool, the precipitate of potassium chloride was filtered off and washed with benzene; 3.6 g was obtained (theoretical amount 3.7 g). The filtrate was dried over calcined sodium sulfate and vacuum-fractionated. Two fractionations yielded 8.15 g (80%) of a substance boiling at 108-109° (4 mm); n_D^{20} 1.5122; d_4^{20} 1.1894; found MR 57.62; calculated MR 57.84.

O,O-Diisopropyl S-Acetyl Phosphorothiolothionate. This was prepared from 12.6 g (0.02 mole) of lead bis[O,O-diisopropyl phosphorothiolothionate] and 6.3 g (0.08 mole) of acetyl chloride, following the procedure used for O,O-diethyl S-acetyl phosphorothiolothionate; 7.0 g (67%) was obtained. O,O-Diisopropyl S-acetyl phosphorothiolothionate is a light-yellow liquid, b.p. 100-101° (3 mm); n_D^{20} 1.4979; d_4^{20} 1.1177; found MR 67.21; calculated MR 67.08.

Found %: P 12.15; 11.95
 $C_8H_{17}O_3PS_2$. Calculated %: P 12.11

O,O-Diisobutyl S-Acetyl Phosphorothiolothionate. This was prepared from 5.28 g (0.02 mole) of sodium O,O-diisobutyl phosphorothiolothionate and 4.71 g (0.06 mole) of acetyl chloride; the yield was 4.0 g (70%). O,O-Diisobutyl S-acetyl phosphorothiolothionate is an orange liquid; n_D^{20} 1.4929; d_4^{20} 1.0793; found MR 76.56; calculated MR 76.62. B.p. 125-126° (3 mm).

Found %: P 10.96; 10.83
 $C_{10}H_{21}O_3PS_2$. Calculated %: P 10.91

O,O-Diisopropyl S-Benzoyl Phosphorothiolothionate. Benzoyl chloride (4.2 g, i.e. 0.03 mole) was added to 8.3 g (0.013 mole) of lead bis[O,O-diisopropyl phosphorothiolothionate]. No appreciable change occurred in the reaction mixture at room temperature. When the mixture was heated in a water bath at 70-80°, the precipitate began to diminish in bulk and turned from gray to white; a layer of colorless liquid appeared above the precipitate. The reaction mixture was heated in a water bath until the liquid above the precipitate began to turn yellow (30 minutes). When cool, the whole of the reaction mixture solidified; it was extracted with ether, and the insoluble residue of lead chloride was filtered off; 4.7 g was obtained (theoretical amount 3.6 g). The filtrate was dried over calcined sodium sulfate, and the ether and excess of benzoyl chloride were distilled off under reduced pressure. The residue crystallized out. Recrystallization from ethanol yielded 6.7 g (80%) of O,O-diisopropyl S-benzoyl phosphorothiolothionate, m.p. 51-52°, in the form of fine prisms, slightly pink-lilac in color. It is readily soluble in acetone, ether, carbon tetrachloride, and petroleum ether; insoluble in water.

Found %: P 9.78; 9.54
 $C_{13}H_{15}O_3PS_2$. Calculated %: P 9.75

Preparation of S-Alkoxy carbonyl Derivatives of O,O-Dialkyl S-Hydrogen Phosphorothiolothionates. An excess of alkyl chloroformate was added to potassium or sodium O,O-dialkyl phosphorothiolothionate. Reaction began at room temperature only in the case of methyl chloroformate: the reaction mixture grew warm, the precipitate rapidly became less in bulk, and a layer of colorless liquid appeared. All the other chloroformic esters, from ethyl to isopentyl, reacted only when heated. The reaction mixture was heated for a period varying from 30 minutes to 3-4 hours at a temperature varying from 90° to 140-150°. The precipitate of potassium or sodium chloride was then filtered off and washed with benzene; in all cases the salt was obtained in quantitative yield. The filtrate was dried over sodium sulfate and fractionated under reduced pressure. Yields of 80-90% were obtained of the S-alkoxycarbonyl derivatives.

O,O-Diethyl S-Methoxycarbonyl Phosphorothiolothionate. A mixture of 11.2 g (0.05 mole) of potassium O,O-diethyl phosphorothiolothionate and 9.4 g (0.1 mole) of methyl chloroformate yielded 10.0 g (82%) of O,O-diethyl S-methoxycarbonyl phosphorothiolothionate, b.p. 105-106° (3.5 mm); n_D^{20} 1.5063; d_4^{20} 1.2171; found MR 59.66; calculated MR 59.48.

Found %: P 12.73; 12.72
 $C_8H_{15}O_4PS_2$. Calculated %: P 12.70

O,O-Diethyl S-Ethoxycarbonyl Phosphorothiolothionate. This was obtained in 91% yield (8.7 g) from 8.4 g (0.037 mole) of potassium O,O-diethyl phosphorothiolothionate and 5.4 g (0.05 mole) of ethyl chloroformate. It had b.p. 115° (4 mm); n_D^{20} 1.5001; d_4^{20} 1.1891; found MR 63.90; calculated MR 64.10.

Found %: P 12.04
 $C_7H_{15}O_4PS_2$. Calculated %: P 12.01

O,O-Diethyl S-Propoxycarbonyl Phosphorothiolothionate. A mixture of 8.4 g (0.037 mole) of potassium O,O-diethyl phosphorothiolothionate and 6.1 g (0.05 mole) of propyl chloroformate yielded 9.1 g (91%) of O,O-diethyl S-propoxycarbonyl phosphorothiolothionate, b.p. 125° (5.5 mm); n_D^{20} 1.4981; d_4^{20} 1.1620; found MR 68.70; calculated MR 68.72.

Found %: C 36.65; 35.60; H 6.45; 6.40
 $C_8H_{17}O_4PS_2$. Calculated %: C 35.27 H 6.25

O,O-Diethyl S-Isobutoxycarbonyl Phosphorothiolothionate. This was prepared from 4.2 g (0.018 mole) of potassium O,O-diethyl phosphorothiolothionate and 5.8 g (0.038 mole) of isobutyl chloroformate. B.p. 162-163° (6 mm); yield 4.3 g (84%); n_D^{20} 1.4889; d_4^{20} 1.1281; found MR 73.25; calculated MR 73.34.

Found %: C 37.98; 37.92; H 6.82, 6.77; P 10.89, 10.87
 $C_9H_{19}O_4PS_2$. Calculated %: C 37.76; H 6.64; P 10.84

O,O-Diethyl S-Isopentyloxycarbonyl Phosphorothiolothionate. A mixture of 4.2 g (0.018 mole) of potassium O,O-diethyl phosphorothiolothionate and 7.5 g (0.05 mole) of isopentyl chloroformate yielded 4.3 g (84%) of O,O-diethyl S-isopentyloxycarbonyl phosphorothiolothionate, b.p. 137-138° (4 mm); n_D^{20} 1.4925; d_4^{20} 1.1179; found MR 78.04; calculated MR 77.96.

Found %: C 40.18; 40.20; H 7.12; 7.15; P 10.23; 10.73
 $C_{10}H_{21}O_4PS_2$. Calculated %: C 40.00; H 7.00; P 10.34

O,O-Diisopropyl S-Ethoxycarbonyl Phosphorothiolothionate. This was prepared from 8.8 g (0.037 mole) of sodium O,O-diisopropyl phosphorothiolothionate and 5.4 g (0.05 mole) of ethyl chloroformate. B.p. 109-109.5° (3 mm); yield 8.5 g (90%); n_D^{20} 1.4894; d_4^{20} 1.1301; found MR 73.18; calculated MR 73.34.

Found %: C 37.92; 38.00; H 6.75; 6.73; P 10.79; 10.84

$C_8H_{18}O_4PS_2$. Calculated %: C 37.76; H 6.64; P 10.84

O,O-Diisopropyl S-Isopentyloxycarbonyl Phosphorothiolothionate. A mixture of 4.4 g (0.018 mole) of sodium O,O-diisopropyl phosphorothiolothionate and 3.8 g (0.025 mole) of isopentyl chloroformate yielded 5.1 g (90%) of O,O-diisopropyl S-isopentyloxycarbonyl phosphorothiolothionate, b.p. 137-138° (3 mm); n_D^{20} 1.4841; d_4^{20} 1.0773; found MR 87.24; calculated MR 87.19.

Found %: P 9.71; 9.74

$C_{12}H_{25}O_4PS_2$. Calculated %: P 9.45

SUMMARY

1. Values of the group refractions of the two atoms of sulfur in esters and mixed anhydrides of phosphorothiolothionic acid have been determined. The values found for AR_{S_2} are: for O,O-dialkyl S-hydrogen phosphorothiolothionates $(RO)_2PSSH$ 18.82; for trialkyl phosphorothiolothionates $(RO)_2PS(SR)$ 18.72; and for O,O-dialkyl S-acyl phosphorothiolothionates $(RO)_2PSSCOX$ 19.77.

2. The syntheses of S-acyl and S-alkoxycarbonyl derivatives of O,O-dialkyl S-hydrogen phosphorothiolothionates have been described.

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* See Consultants Bureau Translation, page 825.

** See Consultants Bureau Translation, page 145.

*** See Consultants Bureau Translation, page 661.

**** See Consultants Bureau Translation, page 109.

ACTION OF ALCOHOLS ON BICYCLIC TERPENE OXIDES

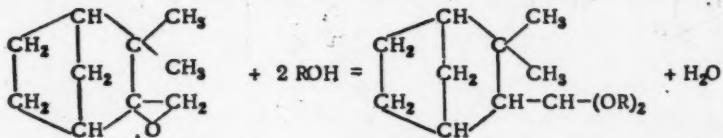
COMMUNICATION 3. ACETALS OF 3-CAMPHENILANE CARBOXALDEHYDE

B. A. Arbuzov and L. A. Mukhamedova

In a previous investigation [1] B. A. Arbuzov and Isaeva have shown that, when primary alcohols react with Δ^3 -carene oxide in presence of sulfuric acid, they add at the oxide ring with formation of monoethers of the carene glycol (4-alkoxy-3-caranols). When the epoxide is treated with secondary alcohols, reaction proceeds in two directions: in addition to the formation of the normal alcohol addition product, the partial isomerization of the epoxide to an unsaturated aldehyde occurs. With a tertiary alcohol Δ^3 -carene oxide reacts with formation only of the unsaturated aldehyde.

The behavior of camphene oxide in this reaction was studied for the case of reaction with methyl alcohol. The main reaction product was the dimethyl acetal of 3-camphenilane carboxaldehyde. In addition, a small amount of the monomethyl ether of the glycol (3-methoxy-3-camphenilane methanol) was isolated. No further study was made of the action of alcohols other than methyl alcohol on camphene oxide and its isomerization product (3-camphenilane carboxaldehyde).

In the present paper we give the results of experiments on the action of alcohols (ethyl, butyl, isobutyl, octyl, and isopropyl) on camphene oxide, and the action of glycols on 3-camphenilane carboxaldehyde. When the primary alcohols reacted with camphene oxide in presence of sulfuric acid, the corresponding acetals of 3-camphenilane carboxaldehyde were obtained:



The constants of the acetals obtained are given in Table 1.

TABLE 1

Acetal of 3-camphenilane-carboxaldehyde	B.p. in °C (p in mm Hg)	n_{D}^{20}	d_4^{20}	MR		Yield %
				Calc'd	Found	
Diethyl	113-114.5 (8.5)	1.4610	0.9414	65.74	65.95	35.9
Dibutyl	149-151 (6.0)	1.4650	0.9264	84.21	84.26	26.2
Diisobutyl	140-141 (7.0)	1.4612	0.9196	84.21	84.28	36.3
Diocetyl	217-218 (4.0)	1.4665	0.8995	121.15	121.50	28.1

The action of isopropyl alcohol on camphene oxide resulted in the formation of the isomerization product of camphene oxide, 3-camphenilane-carboxaldehyde, as shown by the preparation of its semicarbazone.

In presence of sulfuric acid, therefore, camphene oxide is converted into 3-camphenilane carboxaldehyde, which gives acetals with primary alcohols. In the case of a secondary alcohol, acetal formation does not occur. Products formed by the addition of alcohols directly to the oxide ring could not be detected.

All of the acetals of 3-camphenilane carboxaldehyde obtained in this way are colorless liquids having a camphorlike odor. With the object of comparing the odor of these acetals with that of cyclic acetals of 3-camphenilane carboxaldehyde, we prepared some of the latter by the action of glycols on the aldehyde in presence of phosphoric acid. The constants of these acetals are given in Table 2.

All of these cyclic acetals have a camphor odor and are of no interest in perfumery.

TABLE 2

Formula of acetal	B.p. in °C (p in mm Hg)	d_{10}^{20}	d_4^{20}	MR		Yield %
		Cal'd	Found			
	120-121 (14.5)	1.4877	1.0386	54.30	54.44	69.8
	118-119 (12)	1.4805	1.0100	58.92	59.20	86.0
	127.5-128.5 (12)	1.4890	1.0285	58.92	59.03	63.0
	126.5-127.5 (11)	1.4815	1.0013	63.54	63.80	72.0

EXPERIMENTAL

Action of Ethyl Alcohol on Camphene Oxide in presence of Sulfuric Acid. The substances taken for reaction were camphene oxide (15 g), ethyl alcohol (28 g), and sulfuric acid of sp. gr. 1.8 (0.18 g). A solution of the camphene oxide in 9 g of ethyl alcohol was dropped slowly into 19 g of ethyl alcohol containing the sulfuric acid. The temperature of the reaction mixture rose to 40°; when it had fallen again to 18°, the sulfuric acid was neutralized with sodium ethoxide. The alcohol was distilled off, and the residue was vacuum-fractionated from an Arbuzov flask. The following fractions were obtained:

Fraction I	b.p. 86-100°(9 mm);	1.3 g
Fraction II	b.p. 100-114°(8.5 mm);	5 g; n_{D}^{20} 1.4650
Fraction III	b.p. 114-119°(8.5 mm);	7.4 g; n_{D}^{20} 1.4622

Two refractions of Fractions II and III yielded 8 g of a fraction having the following constants: b.p., 113-114.5° (8.5 mm) n_D^{20} 1.4610; d_4^{20} 0.9414; found MR 65.95, calculated at $C_{14}H_{20}O_2$ MR 65.73. It was a colorless, oily liquid, and its constants were not affected by distillation over sodium.

Found %: C 74.15; 74.49; H 11.42; H 11.76
 $C_{14}H_{26}O_2$. Calculated %: C 74.28; H 11.58

In order to compare reaction products, 3-camphenilane carboxaldehyde was treated with ethyl alcohol in presence of sulfuric acid (10 g of the aldehyde and 30 ml of the alcohol). A solution of the 3-camphenilane carboxaldehyde in 10 ml of ethyl alcohol was dropped slowly into 20 ml of ethyl alcohol containing two drops of sulfuric acid. After neutralization of the sulfuric acid with sodium ethoxide and removal of the alcohol, the residue was vacuum-fractionated. Two fractionations yielded 4 g of a product having the following constants: b.p. 113-115° (8.5 mm); n_D^{20} 1.4612; d_4^{20} 0.9418.

Action of Butyl Alcohol on Camphene Oxide in presence of Sulfuric Acid. The substances taken for reaction were camphene oxide (15 g.), butyl alcohol (44 g.), and sulfuric acid of sp. gr. 1.8 (0.18 g.). A solution of

the camphene oxide in 10 g of butyl alcohol was dropped slowly into 34 g of butyl alcohol containing the sulfuric acid. The temperature of the reaction mixture rose to 48°, and when it had returned to that of the room the sulfuric acid was neutralized with sodium butoxide, the alcohol was distilled off under somewhat reduced pressure (200 mm), and the residue was vacuum-fractionated. Two fractionations resulted in the isolation of 7.3 g of a product having the following constants: B.p. 149-151° (6 mm); n_D^{20} 1.4650; d_4^{20} 0.9264; found MR 84.26; calculated at $C_{18}H_{34}O_2$ MR 84.21. It was a colorless, oily liquid having a camphor odor.

Found %: C 76.32; H 11.91
 $C_{18}H_{34}O_2$. Calculated %: C 76.53; H 12.13

Action of Isobutyl Alcohol on Camphene Oxide in presence of Sulfuric Acid. The substances taken for reaction were camphene oxide (15 g), isobutyl alcohol (44 g, i.e. 56 ml), and sulfuric acid of sp. gr. 1.8 (0.17 g). A solution of the camphene oxide in 20 ml of isobutyl alcohol was dropped slowly into 36 ml of isobutyl alcohol containing the sulfuric acid. The temperature of the reaction mixture rose to 50°. After neutralization with sodium isobutoxide and removal of the alcohol, the residue was vacuum-fractionated with the following results:

Fraction I	b.p. up to 138° (8 mm); 3 g;	n_D^{20} 1.4863
Fraction II	b.p. 138 - 140° (8 mm); 5 g;	n_D^{20} 1.4682
Fraction III	b.p. 140 - 143° (8 mm); 9 g;	n_D^{20} 1.4615

Refractionation of Fractions II and III yielded 10.1 g of a fraction having b.p. 140-141° (7 mm); n_D^{20} 1.4612; d_4^{20} 0.9196, Found MR 84.28; calculated at $C_{18}H_{34}O_2$, MR 84.21. The reaction product was a colorless, oily liquid having a camphor odor.

Found %: C 76.18; 76.25; H 12.29; 12.24
 $C_{18}H_{34}O_2$. Calculated %: C 76.53; H 12.13

Action of Isopropyl Alcohol on Camphene Oxide in presence of Sulfuric Acid. The substances taken for reaction were camphene oxide (15 g), isopropyl alcohol (42 g), and sulfuric acid of sp. gr. 1.8 (0.17 g). The procedure was as in the previous experiments. The temperature rose to 40°. After the usual treatment the residue was vacuum-fractionated, and yielded:

Fraction I	b.p. up to 80° (10 mm); 2.3 g
Fraction II	b.p. 80 - 83° (10 mm); 8.1 g
Fraction III	b.p. 83 - 120° (10 mm); 2.3 g
Residue	3.4 g

Fraction II solidified in the condenser.

The Semicarbazone: The substances taken for reaction were the fraction of b.p. 80-83° at 10 mm (1.3 g), semicarbazide hydrochloride (1 g), and sodium acetate (1.5 g). The substance of b.p. 80-83° at 10 mm was added to a solution of the semicarbazide hydrochloride and sodium acetate in a small amount of water, and some methyl alcohol was added to bring the substance into solution. The mixture was shaken vigorously, and a precipitate formed. It was filtered off, washed with water, and dried (2.4 g of crude product). After several recrystallizations from alcohol (methyl and ethyl), the semicarbazone melted at 191-192°. In a mixture melting point test with the semicarbazone of 3-camphenilane carboxaldehyde there was no depression.

Fraction III was not investigated owing to the small amount available and its extended boiling range.

Action of Octyl Alcohol on Camphene Oxide in presence of Sulfuric Acid. The substances taken for reaction were camphene oxide (10 g), octyl alcohol (43 g), and sulfuric acid (a few drops). The procedure was as in the previous experiments. After neutralization of the reaction mixture with sodium octyloxide and removal of excess of octyl alcohol, the residue was vacuum-distilled, and yielded:

Fraction I	b.p. up to 206° (5 mm); 2.9 g;	n_D^{20} 1.4740
Fraction II	b.p. 207 - 216° (5 mm); 1.5 g;	n_D^{20} 1.4712
Fraction III	b.p. 216 - 219° (5 mm); 9.1 g;	n_D^{20} 1.4672

Refractionation of Fraction III yielded 7.3 g of a substance of b.p. 217-218 (4 mm); n_D^{20} 1.4665; d_4^{20} 0.8995; found MR 121.5; calculated at $C_{26}H_{50}O_2$ MR 121.15. It was a colorless, oily liquid having a camphor odor.

and the following formula found to be correct: $C_{12}H_{20}O_2$. Found %: C 78.96; H 13.07. Calculated %: C 79.12, H 12.77

Action of Ethylene Glycol on 3-Camphenilanecarboxaldehyde. A drop of orthophosphoric acid was added to a mixture of 10 g of 3-camphenilanecarboxaldehyde and 4.1 g of ethylene glycol. When the mixture was heated at a little above 100°, elimination of water occurred. The water was driven off, the last traces being removed under reduced pressure. Fractionation gave the following results:

Fraction I	b.p. 100 - 110°;	0.8 g
Fraction II	b.p. up to 90° (11.5 mm);	2.5 g
Fraction III	b.p. 90 - 113° (11.5 mm);	0.3 g; n_D^{20} 1.4940
Fraction IV	b.p. 113 - 117° (11.5 mm);	9 g; n_D^{20} 1.4877
Residue	0.3 g

Refractionation of Fraction IV yielded a product having the following constants: b.p. 120-121° (14.5 mm); n_D^{20} 1.4877; d_4^{20} 1.0386. Found MR 54.44, calculated at $C_{12}H_{20}O_2$ MR 54.30. It was a colorless, oily liquid having an odor reminiscent of camphor.

Found %: C 73.67; 73.33; H 10.35; 10.29
 $C_{12}H_{20}O_2$. Calculated %: C 73.42; H 10.27

Action of 1,2-Propanediol on 3-Camphenilanecarboxaldehyde. A drop of orthophosphoric acid was added to a mixture of 10 g of 3-camphenilanecarboxaldehyde and 5 g of 1,2-propanediol. The procedure was as in the previous experiment. After removal of water, the residue was vacuum-fractionated with the following results:

Fraction I	b.p. 100 - 110°	1.5 g
Fraction II	b.p. up to 80° (13.5 mm);	
Fraction III	b.p. 80 - 119° (13.5 mm);	
Fraction IV	b.p. 119 - 121° (13 mm)	
Residue	0.3 g

Fraction IV was redistilled and yielded a substance having the following constants: b.p. 118-119° (12 mm); n_D^{20} 1.4805; d_4^{20} 1.0100; found MR 59.20; calculated at $C_{13}H_{22}O_2$ MR 58.92. It was a colorless liquid having a camphor odor:

Found %: C 73.81; H 10.69
 $C_{13}H_{22}O_2$. Calculated %: C 74.24; H 10.53

Action of 1,3-Propanediol on 3-Camphenilanecarboxaldehyde. A drop of orthophosphoric acid was added to a mixture of 8.6 g of 3-camphenilanecarboxaldehyde and 4.3 g of 1,3-propanediol. After removal of water, the residue was vacuum-fractionated, and yielded:

Fraction I	b.p. 100 - 110°;	1.5 g
Fraction II	b.p. up to 100°; (12 mm);	
Fraction III	b.p. 100 - 125°; (12 mm);	
Fraction IV	b.p. 125 - 129°; (12 mm);	

Fraction IV was redistilled and yielded a substance having the following constants: b.p. 127.5 - 128.5° (12 mm); n_D^{20} 1.4890; d_4^{20} 1.0285; found MR 59.03, calculated at $C_{13}H_{22}O_2$ MR 58.92. It was a colorless liquid having a camphor odor.

Found %: C 73.91; H 10.46
 $C_{13}H_{22}O_2$. Calculated %: C 74.24; H 10.53

The Action of 1,3-Butanediol on 3-Camphenilanecarboxaldehyde. The substances taken for reaction were 3-camphenilanecarboxaldehyde (8 g), 1,3-butanediol (4.8 g), and orthophosphoric acid (one drop), and the procedure was as in the previous experiments. The results of the fractionation were as follows:

Fraction I	b.p. 100 - 110°; (760 mm);	2.4 g
Fraction II	b.p. up to 100°; (11 mm);	
Fraction III	b.p. 100 - 126°; (11 mm);	0.3 g
Fraction IV	b.p. 126 - 127.5°; (11 mm);	8.5 g
Residue		0.5 g

The constant of Fraction IV were as follows: n_D^{20} 1.4815; d_4^{20} 1.0013; found MR 63.80, calculated at $C_{14}H_{24}O_2$ MR 63.54. It was a colorless liquid having a camphor odor.

Found %: C 74.85; H 10.71
 $C_{14}H_{24}O_2$. Calculated %: C 74.95; H 10.78

SUMMARY

1. A study has been made of the reaction of camphene oxide with primary alcohols (ethyl, butyl, iso-butyl and octyl) and a secondary alcohol (isopropyl) in presence of sulfuric acid. It has been shown that the reaction of camphene oxide with primary alcohol is accompanied by isomerization of the epoxide and formation, as the sole product, of the corresponding acetals of 3-camphenilanecarboxaldehyde.

2. It has been shown that in the case of secondary alcohols, exemplified by isopropyl alcohol, reaction is again accompanied by isomerization, but it stops at the 3-camphenilanecarboxaldehyde stage, and no acetal formation occurs.

3. By the reaction of 3-camphenilanecarboxaldehyde with glycols (ethylene glycol, 1,2-propanediol, 1,3-propanediol, and 1,3-butanediol) in presence of phosphoric acid, the corresponding cyclic acetals of 3-camphenilanecarboxaldehyde have been prepared

LITERATURE CITED

[1] B. A. Arbuzov and Z. G. Isaeva, J. Gen. Chem. 19, 893 (1949).*

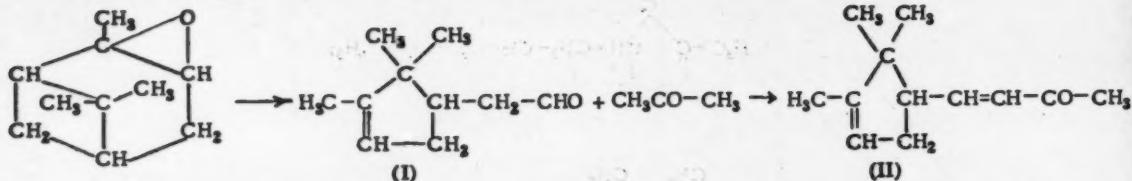
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* See Consultants Bureau Translation, page 881.

On the 10th anniversary of the October Revolution, the authors present this article to the memory of B. A. Arbuzov and L. A. Mukhamedova, who died in 1917. The authors express their thanks to the editors of the journal for their permission to publish this article.

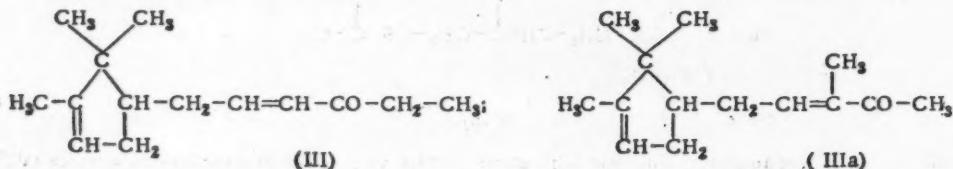
In presence of zinc bromide, α -pinene oxide readily isomerizes to α -campholenaldehyde (I) [1]. Campholenaldehyde is isomeric with the cyclohexanones, but differs greatly in structure from these substances.



It would be expected that the condensation of α -campholenaldehyde with acetone would result in the formation of the ketone II, isomeric with the ionones. In order to determine the relation between structure and odor in compounds isomeric with the ionones, we have carried out the condensation of α -campholenaldehyde with acetone and certain other ketones.*

Condensation of α -campholenaldehyde with acetone in presence of aqueous alkali yielded the ketone II, which contained some of the aldol form as impurity. We could not free the material from the latter completely by distillation, but, when the product was distilled over a crystal of camphorsulfonic acid, water was eliminated and, after further distillations, the ketone II was obtained in the pure state. Its constants are as follows: b.p. 132-134° (10 mm); n_D^{20} 1.4893; d_4^{20} 0.9196; found MR 60.40; calculated at $\text{C}_{13}\text{H}_{20}\text{O}$ \bar{F}_2 MR 59.11; ϵ 1,29. The ketone is an oily liquid having a very slight yellowish-green color and a pleasant odor reminiscent of ionone. The yield of the pure product was 44%. The semicarbazone melted at 136-137°. For the ketone II, B. Sh. Khusnutdinov gave the following constants: b.p. 142° (19 mm); n_D^{20} 1.4835; d_4^{20} 0.9161; MR 59.96; m.p. of semicarbazone 160-161°. These constants, with the exception of the melting point of the semicarbazone, are close to those obtained by us.

The condensation of α -campholenaldehyde with 2-butanone in presence of sodium ethoxide gave poor results. Better results were obtained by the use of aqueous alkali. The reaction product, after removal of the aldol form over camphorsulfonic acid, yielded the ketone $\text{C}_{14}\text{H}_{22}\text{O}$, which had the following constants: b.p. 111.5-113.5° (3 mm); n_D^{20} 1.4910; d_4^{20} 0.9239; found MR 64.68; calculated at $\text{C}_{14}\text{H}_{22}\text{OF}_2$ MR 63.73; ϵ 0.95. Which of the structures III and IIIa represents this ketone was not ascertained; on the basis of the data in the literature [3], the structure III must be regarded as the more probable.



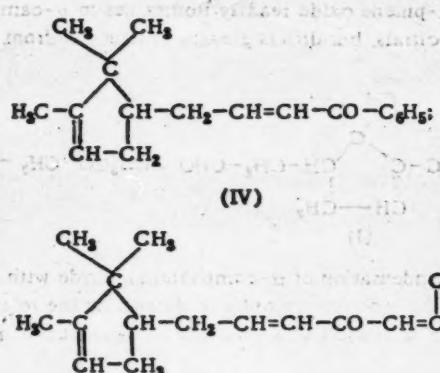
1-(or 3-)Campholen-2-butanone is a greenish liquid having an odor reminiscent of ionone. Its semicarbazone melted at 203-204°. For this ketone Khusnutdinov gives only b.p. 147° (14 mm); d_4^{20} 0.9421 and m.p. of semicarbazone 203-204°. The boiling point of the ketone and its high specific gravity clearly point to aldol impurity, which we succeeded in removing only by distillation over camphorsulfonic acid.

α -Campholenaldehyde readily reacts with acetophenone in presence of aqueous alkali. The condensation product (IV), after removal of aldol, is a yellowish-green oily liquid having a feeble pleasant odor and the following constants: b.p. 165-166.5° (2 mm); n_D^{20} 1.5495; d_4^{20} 0.9986; found MR 81.04; calculated at $\text{C}_{14}\text{H}_{22}\text{OF}_5$ MR 78.60;

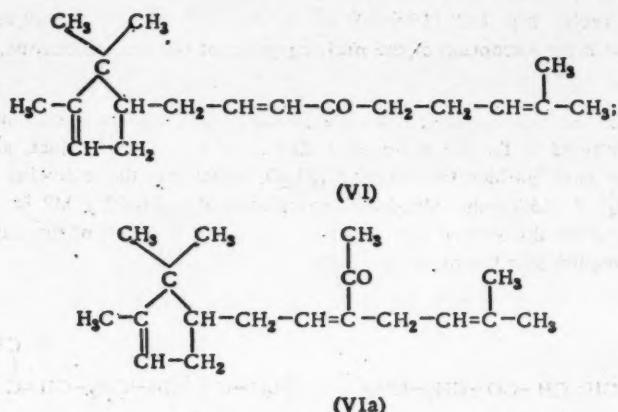
* Some of the syntheses described in this paper were carried out previously in our laboratory by B. Sh. Khusnutdinov, who died in the Great Patriotic War. In his papers there are only a few constants of the compounds, without any description of the conditions of preparation.

ϵ 2.4. For this ketone Khusnutdinov gives the following constants: b.p. 201-202° (12 mm); n_D^{20} 1.5433; d_4^{20} 0.9996, MR 80.2; m.p. of semicarbazone 154-155°.

With mesityl oxide α -campholenaldehyde gave the ketone V, which we did not succeed in obtaining in an analytically pure form. It had the following constants: b.p. 153-155° (6 mm); n_D^{20} 1.5093; d_4^{20} 0.9294; found MR 74.69; calculated for $C_{16}H_{24}O$ \bar{F}_3 , MR 72.49; ϵ 2.20. For the ketone V Khusnutdinov gave rather different constants: b.p. 169-171° (10 mm); n_D^{20} 1.5010; d_4^{20} 0.9312; MR 73.46; ϵ 0.96. Such a low value for the exaltation does not agree with the structure of the ketone V, which contains three conjugated bonds. It is clear that Khusnutdinov's product contained aldol impurity.

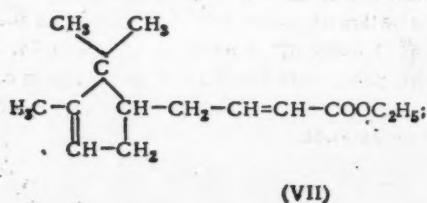


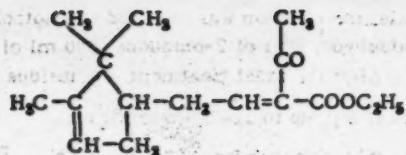
α -Campholenaldehyde was condensed with 6-methyl-5-hepten-2-one in presence of sodium methoxide. The resulting ketone (VI or VIa), which was isolated in low yield, had the following constants: b.p. 164-166° (5 mm); n_D^{20} 1.4950; d_4^{20} 0.9145; found MR 83.10; calculated for $C_{18}H_{28}O$ \bar{F}_3 , MR 81.73; ϵ 1.37. 1-(or 3-)Campholen-6-methyl-5-hepten-2-one has a feeble pleasant odor. Which of the structures VI and VIa represents this ketone was not ascertained; VI appears to be the more probable.



The condensation of α -campholenaldehyde with ethyl acetate yielded ethyl campholenalacetate (VII), which had the following constants: b.p. 126-128° (5 mm); n_D^{20} 1.4745; d_4^{20} 0.9478; found MR 66.00; calculated for $C_{14}H_{22}O_2$ \bar{F}_2 , MR 65.37; ϵ 0.63.

The condensation of α -campholenaldehyde with ethyl acetoacetate yielded ethyl 2-campholenalacetoacetate (VIII), which had the following constants: b.p. 132.5-134.5° (2 mm); n_D^{20} 1.4857; d_4^{20} 0.9910; found MR 76.52; calculated for $C_{16}H_{24}O_3$ \bar{F}_2 , MR 74.62; ϵ 1.90.





(VIII)

EXPERIMENTAL

The α -campholenaldehyde that we used as starting material was obtained by the isomerization of α -pinene oxide in presence of zinc bromide; in its turn, α -pinene oxide was prepared from α -pinene by oxidation with peroxycetic acid in ether solution. The boiling point of the α -campholenaldehyde was 83-84° (13 mm), and it had n_D^{20} 1.4652.

Condensation of α -campholenaldehyde with acetone. To a mixture of 20 g of the aldehyde, 35 g of acetone, and 300 ml of water, 50 ml of 2 N caustic soda was added. The reaction mixture was shaken mechanically for 60 hours. The mixture was neutralized with tartaric acid and extracted with ether. The ether extract was dried with calcined sodium sulfate, and the ether was drawn off under somewhat reduced pressure. Vacuum fractionation of the residue from an Arbuzov flask yielded the fractions:

Fraction I, b.p. up to 100° (10 mm); 2 g; n_D^{20} 1.4812

Fraction II, b.p. 100-131° (10 mm); 5 g; n_D^{20} 1.4833

Fraction III, b.p. 131-146° (10 mm); 12.8 g; n_D^{20} 1.4882

Residue: 2.1 g of resinous material

Fraction III was refluxed in presence of camphorsulfonic acid, when the formation of water drops in the condenser was noted. The following fractions were obtained:

Fraction I, b.p. up to 131.5° (9 mm); 1.2 g; n_D^{20} 1.4870

Fraction II, b.p. 131-133.5° (9 mm); 11 g; n_D^{20} 1.4892

A further fractionation yielded a product having the following constants: b.p. 132-134° (10 mm); n_D^{20} 1.4893; d_4^{20} 0.9196; found MR 60.40; calculated for $C_{13}H_{20}O$ F₂ MR 59.11; ϵ 1.29. It was an oily liquid having a feeble yellowish-green color and a pleasant odor, reminiscent of ionone.

Found %: C 80.78; H 10.47
 $C_{13}H_{20}O$. Calculated %: C 81.17; H 10.48

Preparation of the semicarbazone. The substances taken for reaction were semicarbazide hydrochloride (1 g), sodium acetate (1.5 g), and the condensation product from acetone and α -campholenaldehyde (1.7 g); and 2.1 g of crude semicarbazone was obtained. After four recrystallizations from ethyl and methyl alcohols, the semicarbazone melted at 136-137°. A fifth recrystallization had no effect on the melting point. Since the melting point of this semicarbazone was close to that of the semicarbazone of the original aldehyde (the melting point of the semicarbazone of α -campholenaldehyde is 137-138°), the melting point of a mixture was determined; it showed a depression of about 20°. Analysis of the semicarbazone for nitrogen by Dumas' method gave the following results:

Found %: N 17.19
 $C_{14}H_{25}ON_3$. Calculated %: N 16.86

Condensation of α -campholenaldehyde with 2-butanone. A solution of 2 g of sodium in 40 ml of ethyl alcohol was added to a mixture of 17 g of the aldehyde and 8 g of 2-butanone. The solution rapidly turned dark red, and its temperature rose to 50°. Two minutes after the addition of the ethoxide solution, the mixture was neutralized with tartaric acid. After dilution with water, the reaction mixture was extracted with ether, and the ether layer was dried with sodium sulfate. After removal of ether by suction, the residue was vacuum-fractionated, and yielded:

Fraction I, b.p. up to 141° (10 mm); 4 g

Fraction II, b.p. 141-143° (10 mm); 2.5 g; n_D^{20} 1.4860

Fraction III, b.p. 143-155° (10 mm); 1.7 g; n_D^{20} 1.4868

Residue: 12.5 g

In view of the unsatisfactory yield, the reaction was repeated by another method. The reaction mixture, which was prepared from 17 g of the aldehyde, 30 g of 2-butanone, 300 ml of water and 45 ml of 2 N caustic soda, was shaken mechanically for 60 hours. After the usual treatment, the residue was vacuum-fractionated, and yielded:

Fraction I, b.p. up to 124° (4.5 mm); 8 g

Fraction II, b.p. 125-132° (4.5 mm); 13.6 g; n_D^{20} 1.4885

Residue: 1.2 g

Fraction II was distilled with camphorsulfonic acid, and an appreciable number of water drops were observed in the condenser tube. A further fractionation yielded 10.3 g of a product having the following constants: b.p. 111.5-113.5° (3 mm); n_D^{20} 1.4910; d_4^{20} 0.9239; found MR 64.68; calculated for $C_{14}H_{22}O$ \bar{F}_2 MR 63.73; ϵ 0.95. It was a slightly greenish, oily liquid having an odor of cedarwood. After dilution, it had an odor reminiscent of ionone.

Found %: C 81.43; H 10.92

$C_{14}H_{22}O$. Calculated %: C 81.52; H 10.75

Preparation of the semicarbazone. The substances taken for reaction were semicarbazide hydrochloride (1 g), sodium acetate (1.5 g), and the condensation product from α -campholenaldehyde and 2-butanone (1.8 g); and after 30 minutes the semicarbazone was precipitated. It was filtered off, washed with water, and dried (2.8 g of crude product). After three recrystallizations, the semicarbazone melted at 203-204°. A fourth recrystallization had no effect on the melting point. Analysis of the semicarbazone for nitrogen by Dumas' method gave the following results:

Found %: N 16.26

$C_{15}H_{25}ON_3$. Calculated %: N 15.95

Condensation of α -campholenaldehyde with acetophenone. To a mixture of 18.7 g of the aldehyde, 25 g of acetophenone, and 300 ml of water, 50 ml of 2 N caustic soda was added. The reaction mixture was shaken mechanically for 75 hours. After neutralization with tartaric acid, the solution was extracted with ether, and the ether layer was dried with sodium sulfate. After removal of ether under suction, the residue was vacuum-fractionated, and yielded:

Fraction I, b.p. up to 100° (13 mm); 20 g

Fraction II, b.p. 100-170° (13-6 mm); 3.7 g; n_D^{20} 1.5130

Fraction III, b.p. 170-190° (6 mm); 12.4 g; n_D^{20} 1.5430

Residue: 1.5 g

Fraction I consisted of unchanged starting materials. Fractions II and III were redistilled with camphorsulfonic acid. As a result of a third distillation 9.6 g of a product was obtained having the following constants: b.p. 165-166.5° (2 mm); n_D^{20} 1.5495; d_4^{20} 0.9986; found MR 81.04; calculated for $C_{18}H_{22}O$ \bar{F}_5 MR 78.60; ϵ 2.4. It was an oily liquid, yellowish-green in color, and having a feeble spicelike odor.

Found %: C 84.60; H 9.07

$C_{18}H_{22}O$. Calculated %: C 85.04; H 8.72

Condensation of α -campholenaldehyde with mesityl oxide. Sodium methoxide (0.2 g of sodium in 2 ml of methyl alcohol) was added to a mixture of 17.5 g of the aldehyde and 14 g of mesityl oxide. The temperature in the reaction flask rose to 62°. After three minutes the solution was neutralized with tartaric acid, diluted with water, and extracted with ether. The ether layer was dried with sodium sulfate. After removal of ether under suction, the residue was vacuum-fractionated, and yielded:

Fraction I, b.p. up to 100° (7 mm); 4.9 g

Fraction II, b.p. 100-161° (8 mm); 4.0 g; n_D^{20} 1.4855

Fraction III, b.p. 161-169° (8 mm); 6.5 g; n_D^{20} 1.4995

Fractions II and III were distilled with camphorsulfonic acid. A further fractionation of these fractions gave 5.1 g of a substance having the following constants: b.p. 153-155° (6 mm); n_D^{20} 1.5093; d_4^{20} 0.9294; found MR 74.69; calculated for $C_{16}H_{24}O$ \bar{F}_3 MR 72.49; ϵ 2.20. It was a yellow, oily liquid having a feeble, spicelike odor.

Found %: C 82.12; 82.22; H 10.61, 10.68

$C_{16}H_{24}O$. Calculated %: C 82.70; H 10.41

Condensation of α -campholenaldehyde with 6-methyl-5-hepten-2-one. The substances taken for reaction were the aldehyde (19 g), the methylheptenone (17 g), water (300 ml), and 2 N caustic soda (50 ml). The reaction mixture was agitated mechanically for 77 hours, and was then neutralized with tartaric acid and extracted with ether. The ether layer was dried with sodium sulfate. The ether was removed under suction, and the residue was vacuum-fractionated, yielding:

Fraction I, b.p. 61-110° (10-5 mm); 21.4 g

Fraction II, b.p. 110-158° (4 mm); 2.2 g

Fraction III, b.p. 158-170° (4-7 mm); 9.2 g; n_D^{20} 1.4840

There was a small amount of resinous residue. Fraction III was fractionated three times more (once with camphorsulfonic acid), but on every occasion partial decomposition occurred, even when an initial residual pressure of 2 mm was attained. As a result, the distillate was contaminated with decomposition products. The resulting product boiled at 146-151° (4-4.5 mm).

In order to obtain the substance in the pure state, the reaction was repeated. To the 21.4 g of Fraction I, b.p. 61-110° (10 mm), which consisted mainly of a mixture of the starting materials, a solution of 0.2 g of sodium in methyl alcohol (2 mm) was added. The temperature rose from 18° to 52°. After three minutes the solution was neutralized with tartaric acid. The mixture was extracted with ether, and the ether layer was dried. After removal of ether under suction, the residue was vacuum-fractionated from an Arbuzov flask in presence of a crystal of camphorsulfonic acid. The following fractions were obtained:

Fraction I, b.p. up to 160° (4-5 mm); 7 g

Fraction II, b.p. 160-180° (5-9 mm); 6.2 g; n_D^{20} 1.4800

Fraction III, b.p. 180-184° (9-10 mm); 3.4 g; n_D^{20} 1.4950

A small amount of resinous material remained as residue. It was not found possible to obtain a pure product from Fraction II, since decomposition occurred during distillation. The constants of Fraction III were as follows: n_D^{20} 1.4950; d_4^{20} 0.9160; found MR 83.40; calculated for $C_{18}H_{28}O_2$ MR 81.73; ϵ 1.37. Fraction III was redistilled, and yielded:

Fraction I, b.p. 164° (5 mm)

Fraction II, b.p. 164-166° (5 mm); 2.1 g

The constants of the substance of b.p. 164-166° (5 mm) were as follows: n_D^{20} 1.4950; d_4^{20} 0.9145; found MR 83.10; calculated for $C_{18}H_{28}O_2$ MR 81.73; ϵ 1.37. It was a colorless, or very slightly yellowish, liquid having a faint pleasant odor.

Found %: C 83.16; H 11.24

$C_{18}H_{28}O_2$. Calculated %: C 83.01; H 10.84

Condensation of α -campholenaldehyde with ethyl acetate. Sodium dust (6 g) was prepared under toluene. The toluene was poured off, and 128 ml of ethyl acetate, previously cooled to a temperature of -10 to -15°, was poured over the sodium. The contents of the flask were cooled to -10 to -15°, and the aldehyde (20 g) was dropped in over a period of one hour. The temperature of the cooled mixture was not allowed to rise above -10°. When the whole of the sodium had dissolved, 18 ml of glacial acetic acid was added, and the mixture was carefully diluted with water. The ethyl acetate layer was separated, and the aqueous layer was extracted with ether. The united extracts were washed with dilute hydrochloric acid, with water, with a very dilute solution of sodium bicarbonate, and again several times with water. The solution was dried with sodium sulfate, solvent was distilled off, and the residue was vacuum-fractionated, yielding:

Fraction I, b.p. up to 115° (10 mm); 3.1 g

Fraction II, b.p. 115-135° (9.5 mm); 1.2 g; n_D^{20} 1.4685

Fraction III, b.p. 136-139° (9.5 mm); 8.5 g; n_D^{20} 1.4740

Residue: 8.9 g of resin

Fraction III was redistilled, and yielded 6.8 g of an ester having the following constants: b.p. 126-128° (5 mm); n_D^{20} 1.4745; d_4^{20} 0.9478; found MR 66.00; calculated for $C_{14}H_{22}O_2$ MR 65.37; ϵ 0.63.

Found %: C 75.46; H 9.99

$C_{14}H_{22}O_2$. Calculated %: C 75.62; H 9.98

Condensation of α -campholenaldehyde with ethyl acetoacetate. A mixture of 22 g of α -campholenaldehyde and 19 g of ethyl acetoacetate was cooled to -15° , and 1.5 g of piperidine was added. The mixture was allowed to stand in the cold. After 48 hours, the mixture was neutralized with dilute sulfuric acid, washed with water, and extracted with ether. The ether layer was dried with sodium sulfate. After removal of ether under suction, the residue was vacuum-fractionated, and yielded:

Fraction I, b.p. up to 115° (5 mm)

Fraction II, b.p. $115-157^{\circ}$ (5 mm); 1 g; n_D^{20} 1.4770

Fraction III, b.p. $157-162^{\circ}$ (6 mm); 17.2 g; n_D^{20} 1.4825

Residue: 7 g of resin

After three fractionations, Fraction III yielded the condensation product (12.9 g), which had the following constants: b.p. $132.5-134.5^{\circ}$ (2 mm); n_D^{20} 1.4857; d_4^{20} 0.9910; found MR 76.52; calculated for $C_{16}H_{24}O_3$ F₂ MR 74.62; ϵ 1.90. It was a faintly yellowish, oily liquid of pleasant odor.

Found %: C 72.38; 72.43; H 9.29; 9.49

$C_{16}H_{24}O_3$. Calculated %: C 72.69; H 9.15

SUMMARY

1. By the condensation of α -campholenaldehyde in alkaline medium with acetone, 2-butanone, acetophenone, mesityl oxide, and 6-methyl-5-hepten-2-one, the corresponding unsaturated ketones have been prepared. In spite of the considerable difference from the isomeric ionones in structure, campholenalacetone has an odor close to that of the ionones. The other ketones have pleasant spicelike odors.

2. α -Campholenaldehyde condenses with ethyl acetate and with ethyl acetoacetate yielding ethyl campholenacetate and ethyl 2-campholenacetate, respectively.

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**DETERMINATION OF THE INDIVIDUAL HYDROCARBON COMPOSITION OF GASOLINES
BY THE COMBINATION METHOD**

COMMUNICATION 4. GASOLINE FROM TUIMAZIN PETROLEUM*

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In this paper we present the results of a study of the individual composition of a gasoline having a boiling limit of 150° from low-sulfur Tuimazin petroleum (Devonian level). The investigation was carried out by the previously described combination method [1], which has been used in the study of two gasolines from Kazanbulak [2] and two Surakhan gasolines [3]. Unlike the Surakhan gasolines, the gasoline studied in the present investigation was obtained directly from the petroleum by distillation in the laboratory, as also were the Kazanbulak gasolines. On account of the increase in the number of hydrocarbons that have now been synthesized and studied spectrographically, and also on account of the perfection of the technique in its separate stages, we have succeeded in accounting for the hydrocarbon composition of the gasoline more completely and in reducing the time required in the actual investigation. Also, in this and subsequent investigations, with the object of improving the optical method and making it more rapid, we have introduced a photoelectric method [4] for measuring the intensities of the Raman lines. Parallel determinations by the photographic and photoelectric methods of measurement for a number of fractions gave satisfactorily agreeing results.

TABLE 1

Distribution by Classes by the Hydrocarbons Found

Class of hydrocarbon	No. of hydrocarbons in the gasoline
Paraffins	20
Cyclopentanes	5
Cyclohexanes	13
Aromatics	6
	44

As a result of this investigation, the gasoline from Tuimazin petroleum has been accounted for to the extent of 87.9% (by weight on the whole gasoline). Altogether, forty-four hydrocarbons have been found in this gasoline, and their contents have been determined quantitatively. Their distribution by classes is given in Table 1.

In what follows, the gasoline from Tuimazin petroleum will be denoted by TsT-2. The letters used to denote the fractions are the same as those used in the papers referred to above [1, 2, 3]. The contents of all of the individual hydrocarbons found in the gasoline have been calculated as percent by weight of the "whole gasoline", and the values are given in Table 2. In the same table the general quantitative balance sheet of

the whole investigation is given. The results in Table 2 permit the group composition of the gasoline to be determined, taking into separate account the normal and branched paraffins, and also the cyclopentane and cyclohexane hydrocarbons. This is shown in Table 3.

As can be seen from Table 2 and 3, the gasoline TsT-2 contains 66.2% of paraffins and 16.5% of naphthene hydrocarbons. Of the paraffin-naphthene part of the gasoline TsT-2, 80% consists of paraffins. Hence, the gasoline from Tuimazin petroleum is a paraffin-base gasoline in composition; also, 59.5% of the paraffin component consists of normal paraffins.

The ratio of the amounts of cyclopentane and cyclohexane hydrocarbons in the naphthene part is 0.48.

The branched-paraffin component is made up of 97.5% of paraffins having a tertiary carbon, and only 2.5% of paraffins having a quaternary carbon. Hence, hydrocarbons having a tertiary carbon predominate among the branched paraffins. Also, among paraffins having tertiary carbon atoms, there is a complete absence in the gasoline TsT-2 of hydrocarbons having two or three tertiary carbon atoms.

When the paraffin composition is examined by groups of hydrocarbons of equal molecular weight, it will be seen that, of the C₅ and C₆ hydrocarbons, the gasoline contains all possible isomers except 2,3-dimethylbutane. Of the C₇ hydrocarbons, all the dimethylpentanes and 3-ethylpentanes are absent in the gasoline TsT-2. Of the C₈

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TABLE 2

Individual Hydrocarbons Found in the Gasoline TsT-2

Hydrocarbon	Content (% by weight)	Hydrocarbon	Content (% by weight)
Paraffin Hydrocarbons			
Propane	0.98	Heptane	9.74
Butane	4.69	2-Methylhexane	2.47
Isobutane	0.70	3-Methylhexane	3.43
Pentane	6.32	Octane	7.12
2-Methylbutane	3.57	2-Methylheptane	4.69
Neopentane (?)	0.49	3-Methylheptane	1.71
Hexane	8.43	4-Methylheptane	0.80
2-Methylpentane	3.06	Nonane	2.05
3-Methylpentane	2.40	3-Methyloctane	1.18
2,2-Dimethylbutane	0.17	4-Methyloctane	2.15
Total			66.2
Cyclopentane Hydrocarbons			
Cyclopentane	0.37	cis-1,2-Dimethylcyclopentane	0.48
Methylcyclopentane	2.44	trans-1,2-Dimethylcyclopentane	1.36
Ethylcyclopentane	0.72		
Total			5.4
Cyclohexane Hydrocarbons			
Cyclohexane	1.21	1-Ethyl-2-methylcyclohexane	0.09
Methylcyclohexane	3.74	1-Ethyl-3-methylcyclohexane	0.25
Ethylcyclohexane	0.70	1-Ethyl-4-methylcyclohexane	0.12
1,1-Dimethylcyclohexane	0.13	1,1,3-Trimethylcyclohexane	2.68
1,2-Dimethylcyclohexane	0.49	1,2,4-Trimethylcyclohexane	0.09
1,3-Dimethylcyclohexane	1.10	1,3,5-Trimethylcyclohexane	0.03
1,4-Dimethylcyclohexane	0.43		
Total			11.1
Aromatic Hydrocarbons			
Benzene	0.53	Accounted for (% on TsT-2)	87.9
Toluene	1.85	Not accounted for	2.3
Ethylbenzene	0.53	Sulfur compounds and losses	1.6
<i>o</i> -Xylene	0.59	Residues in flasks after fractionation	2.5
<i>m</i> -Xylene	1.26	Losses	5.7
<i>p</i> -Xylene	0.42		
Total			100.0

TABLE 3

Group Composition of the Gasoline TsT-2

Class of hydrocarbons	Content (% on TsT-2)
Normal paraffins	39.3
Paraffins having a tertiary carbon	26.2
Paraffins having a quaternary carbon	0.7
Cyclopentanes	5.4
Cyclohexanes	11.1
Aromatics	5.2

hydrocarbons, octane and all three methylheptanes are present. The more branched octane isomers are absent from the gasoline. Of the C₉ paraffins, only three were found; nonane and 3- and 4-methyloctanes.

The content of cyclopentane hydrocarbons in the gasoline TsT-2 is low, and has the value 5.4%. The content of cyclopentane itself is extremely low (0.37%). Among the cyclopentane hydrocarbons having one side chain there is a predominance of methylcyclopentane, and among those having two side chains, only cis- and trans-1,2-dimethylcyclopentanes are found in the gasoline TsT-2, the trans-form predominating. It should be noted that there is an increase of the percent content of cyclopentane hydrocarbons with increase in their molecular weights.

The content of cyclohexane hydrocarbons in the gasoline TsT-2 is 11.1%. The comparatively high content of methylcyclohexane (3.7%) with respect to the other members of this class is noteworthy.

Of the cyclohexanes containing two methyl groups, 1,3-dimethylcyclohexane is present in the greatest amount, and 1,2- and 1,4-dimethylcyclohexanes are present in equal amounts. Among the ethylmethylcyclohexanes, again there is an appreciable predominance of the hydrocarbon with side chains in 1,3-orientation. Among trimethylcyclohexanes, 1,1,3-trimethylcyclohexane, which has a quaternary carbon atom, predominates in the gasoline.

The content of aromatic hydrocarbons in the gasoline TsT-2 is 5.2%, and is close to the content of cyclopentane hydrocarbons (5.4%). In order of reducing contents, the individual aromatic hydrocarbons fall into the following series: toluene, m-xylene, o-xylene, ethylbenzene, benzene, and p-xylene. As in the case of the cyclohexane hydrocarbons, there is a predominance of aromatic hydrocarbons having one side chain, or two in meta orientation. Also, as in the case of the cyclopentane hydrocarbons, the percent content of the aromatic hydrocarbons rapidly increases with increase in molecular weight.

EXPERIMENTAL

Preparation of the wide fraction ShT-2, and its fractionation. The petroleum was distilled from copper vessels, and yielded Fraction Sh, with a boiling limit of 200°. The gaseous hydrocarbons that came off were collected in traps cooled to -70°, and at the end of the fractionation they were united to the distillate. Fraction ShT-2

(boiling limit 200°) so obtained, had the following properties: n_D^{20} 1.4087; d_4^{20} 0.7279; aniline point 59.1°; sulfur content 0.059% by weight.*

The results obtained in the fractionation of the wide fraction through a 25-plate column are given in Table 4 and Fig. 1.

The fraction AT-2 had the following properties: n_D^{20} 1.4036; d_4^{20} 0.7186; aniline point 57.6°; sulfur content 0.0095% by weight. From this point on, all calculations on the contents of individual hydrocarbons and fractions obtained at various stages of the investigation were based on the "whole" gasoline, TsT-2, which consisted of Fractions K₁, L, and A, i.e., all that comes over below 150°. In this investigation, the amount of TsT-2 was 1088.6 g.

Investigation of the gases and the light fraction. The gaseous part K₁T-2 and the light fraction LT-2 contained sulfur compounds. In order to remove the readily volatile sulfur compounds, the tube containing the gaseous part K₁T-2 was connected to a system consisting of a train of wash-vessels containing concentrated solutions

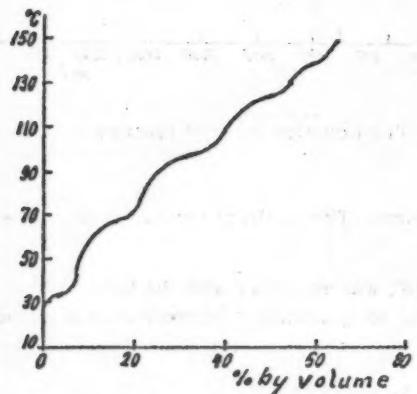


Fig. 1: Fraction curve for the gasoline ShT-2

TABLE 4

Fractionation of the Gasoline ShT-2

Fraction	Boiling limits (°C at 760 mm)	Weight (g)	Content of fraction (% by weight)	
			in ShT-2	in TsT-2
Amount taken for fractionation...	-	1518	100.00	
Gaseous part K ₁ T-2	-	99.6	6.56	9.15
Light fraction LT-2	19.6-44.0	100	6.59	9.19
Main fraction AT-2	44.0-150	889	58.56	81.66
Residue	Above 150	403	26.55	
Losses	-	26.4	1.74	

* The sulfur content was determined by the lamp combustion method.

of caustic soda and sulfuric acid, a silica-gel tower, and some traps in the form of coils cooled by liquid air. The gases were slowly passed through this system and condensed in the traps. In order to expel the gaseous hydrocarbons, nitrogen was passed through the system. The tube and traps were weighed before and after the experiment. A tube containing Fraction LT-2 was then attached to the system, and toward the end of the experiment the tube was heated to 30°. The gas evolved was collected in the same traps together with the gas from the gaseous fraction K_1T-2 , and this gas also was expelled from the system with nitrogen. The united purified gases were denoted by K_1' , and the united unevaporated residues were denoted by L' . The results of the experiments on the purification of the gases of Fractions K_1T-2 and LT-2 from sulfur compounds are given in Table 5.

TABLE 5

Purification of the Gases of K_1T-2 from Sulfur Compounds

Fraction	Weight (g)			Content of fraction (% by weight)	
	K_1T-2	LT-2	total	in $K_1 + L$	in $TsT-2$
Amount taken for purification	49.8	50.0	99.8	100.0	18.33
Gas K_1'	37.3	0	37.3	37.37	6.85
Light fraction $L'T-2$	11.0	49.96	60.96	61.08	11.20
Sulfur compounds and losses	1.5	0.04	1.54	1.54	0.28

TABLE 6

Fractionation of the Gas $K_1'T-2$

Hydrocarbon	Weight (g)	Content of hydrocarbons (% by weight)	
		in $K_1'T-2$	in $TsT-2$
Amt. taken for fractionation	8.0	100.0	6.85
Propane	1.146	14.32	0.98
Isobutane	0.813	10.16	0.70
Butane	4.944	61.80	4.24
Neopentane (?)	0.144	1.80	0.12
Residue of b.p. above 16°	0.77	9.62	0.66
Losses	0.18	2.30	0.15

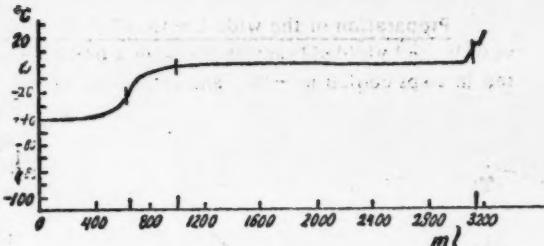


Fig. 2. Fractionation curve of Fraction $K_1'T-2$.

The purified gas $K_1'T-2$ was fractionated through a Podbielnik column. The results of the fractionation are given in Table 6 and in Fig. 2.

The residue from the fractionation of the gas, which boiled above 16°, was not united with the light fraction $L'T-2$ (as required by the scheme [1]) owing to the small amount obtained. Its quantitative composition was assessed on the basis of its refractive index, which was found to be n_D^{20} 1.3541, indicating that the residue contained:

	(% by weight)	
	in residue	in $TsT-2$
Isopentane	88.85	0.59
Pentane	11.15	0.07

The light fraction $L'T-2$ also contained sulfur compounds, and these were removed by an adsorption method. The fraction was passed at -10 to -45° through an adsorption column filled with silica gel, and was eluted with alcohol. The results of these experiments are given in Table 7.

The removal of gas (debutanization) from the desulfurized light fraction was also carried out through a Podbielnik column. The results of the fractionation are given in Table 8.

Investigation of the debutanized Fraction MT-2. Fraction MT-2 was fractionated through a 40-plate column, the fractionation curve (Fig. 3) being determined at the same time. The amounts of the fractions and their properties are given in Table 9.

TABLE 7

Adsorption Separation of Sulfur Compounds
from the Light Fraction L'T-2

Fraction	Weight (g)	Content of fraction (% by weight)	
		In fraction L'T-2	In TsT-2
Amt. of L'T-2 passed	60.96	100.0	11.20
Desulfurized light fraction, L' ¹ T-2	58.28	95.60	10.71
Sulfur compounds and losses	2.68	4.40	0.49

TABLE 8

Debutanization and Fractionation of the Desulfurized Light Fraction L'¹T-2

Hydrocarbon	Weight (g)	Content of hydro- carbon (% by weight)	
		In L' ¹ T-2	In TsT-2
Amt. taken for fractionation	58.3	100.0	10.71
Butane	1.60	2.74	0.29
Neopentane (?)	2.01	3.45	0.37
Debutanized light fraction MT-2	54.13	92.85	9.94
Losses	0.59	0.96	0.11

TABLE 9

Fractionation of the Light Fraction MT-2

Fraction No.	Boiling limits in °C (760 mm)	Weight (g)	n _D ²⁰	d ₄ ²⁰	Aniline point (°C)	Content of fraction (by weight)	
						In MT-2	In TsT-2
	Amt. taken for fractionation	51.10	—	—	—	100.0	9.94
I	Butane (in trap)	0.80	—	—	—	1.57	0.16
I	25.0-32.0	15.30	1.3537	0.6187	76.9	29.94	2.98
II	32.0-36.05	24.35	1.3580	0.6255	70.8	47.65	4.74
Residue	5.4	1.3673	0.6454	65.0	10.57	1.05	
Losses	5.25				10.27	1.02	

As will be seen from Table 9, the constants of Fraction I correspond exactly to those of pure 2-methylbutane (b.p. 27.85°; n_D²⁰ 1.3537 and d₄²⁰ 0.6197), and the constants of Fraction II are close to those of pure pentane (b.p. 36.07°; n_D²⁰ 1.3575; d₄²⁰ 0.6262). The amounts of these fractions, therefore, correspond to the contents of these hydrocarbons in the gasoline.

The residue from Fraction MT-2 was shown by Raman spectra investigation to contain:

	In residue (%)	In TsT-2 (%)
Pentane	65	0.68
2,2-Dimethylbutane	10	0.10
2-Methylpentane	10	0.10
Cyclopentane	15	0.16

Separation of the aromatic hydrocarbons from the mixture of paraffins and naphthenes in the main fraction AT-2. Fraction AT-2 was subjected to chromatographic adsorption separation with the aid of silica gel into aromatics (BT-2) and the paraffin-naphthene part (VT-2). Since the content of aromatics in Fraction AT-2 was low (10% by volume), an intermediate fraction was taken in the adsorption separation. In order to effect complete separation, the intermediate fraction was again subjected to chromatographic adsorption, pentane being used as displacing liquid. The results of the separation are given in Table 10.

In Table 10 both the actual and the corrected amounts of the fractions are given; the latter are obtained from the former by addition of the actual amounts of the fractions that were used for the qualitative tests for aromatic hydrocarbons and for refractive index determinations.

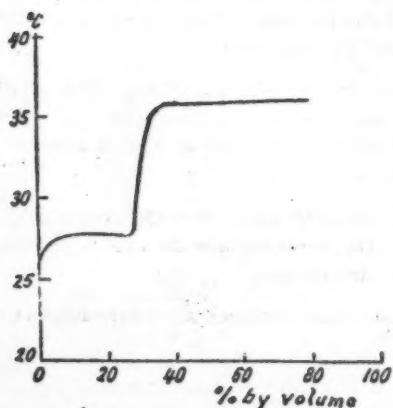


Fig. 3. Fractionation curve of Fraction MT-2

TABLE 10

Chromatographic Resolution of Fraction AT-2

Amt. of Fraction	Separation results											
	Aromatics BT-2				Paraffin-naphthalene part VT-2				Losses			
	actual (g)	corr. (g)	% in AT-2	% in TsT-2	actual (g)	corr. (g)	% in AT-2	% in TsT-2	(g)	% in AT-2	% in TsT-2	
785.2	49.1	51.9	6.6	5.39	723.7	725.07	92.3	75.41	8.3	1.1	0.86	

The fractions isolated had the following properties:

	n_D^{20}	d_4^{20}	Aniline point (°C)	Sulfur content (% by weight)
BT-2	1.4946	0.8617	—	~0.02
VT-2	1.3983	0.7096	63.7	0

The dearomatized fraction did not contain sulfur. The aromatic fraction BT-2 contained about 0.02% of sulfur, i.e., about 7% of the whole of the sulfur contained in the original gasoline AT-2.

Investigation of the aromatics BT-2. The aromatic hydrocarbons BT-2 were fractionated through a column having an efficiency of about 40 theoretical plates. The fractions corresponding to benzene, toluene, and the xylenes were separated, and the fractionation curve was determined at the same time (Fig. 4). The xylene fraction was investigated with the aid of Raman spectra. The results of the fractionation, the properties of the fractions, and the results of the optical analysis are given in Table 11. In order to drive the whole of the xylene fraction from the flask, towards the end of the distillation some pure decahydronaphthalene was added.

Results of the optical analysis of Fraction III

	Content of hydrocarbons (% by wt.)	
	In Fraction III	In TsT-2
o-Xylene	21	0.59
m-Xylene	45	1.26
p-Xylene	15	0.42
Ethylbenzene	19	0.53

It can be seen from these results that, in accordance with its physical properties, Fraction I can be regarded as the benzene fraction, and Fraction II as the toluene fraction. It may, therefore, be assumed that the amounts of these fractions correspond to the contents of benzene and toluene in the gasoline. The presence of sulfur compounds in the fractions of the aromatics BT-2 interfered with the precision of the fractionation and affected the constants of the separated hydrocarbons.

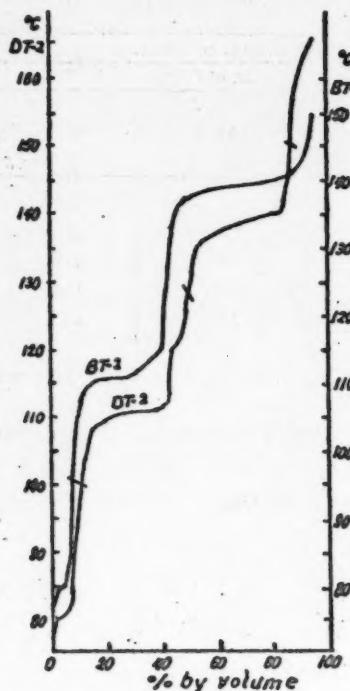


Fig. 4. Fractionation curves of the aromatic fractions BT-2 and DT-2.

Dehydrogenation of the cyclohexane hydrocarbons. The paraffin-naphthalene fraction VT-2 was subjected to catalytic dehydrogenation in order to convert cyclohexane hydrocarbons into aromatics. The fraction VT-2 was passed continuously over an iron-platinum catalyst at 300° at a space velocity of 0.8-1.0 for 24 hours. The results obtained are given in Table 12

In Table 12 the corrected amounts of the catalyst GT-2 were obtained by addition of the amounts of GT-2 used for refractive index determinations to the actual amounts of GT-2. The losses include the hydrogen separating during dehydrogenation of cyclohexane hydrocarbons; the amount was not determined.

The physical properties of the original Fraction VT-2 and of the catalyzate obtained after dehydrogenation (GT-2) were as follows:

	n_D^{20}	d_4^{20}	Aniline point (°C)
VT-2	1.3983	0.7096	63.7
GT-2	1.4040	0.7165	57.1

TABLE 11

Fractionation of the Aromatics BT-2

TABLE 11

Fraction No.	Boiling limits in °C (760 mm)	Weight (g)	n_{D}^{20}	d_4^{20}	Content of fraction (by weight)	
					in BT-2	in TsT-2
Amount taken for fractionation	48.5	48.5	1.4946	0.8617	100.0	5.39
I	76.7-99.9	4.8	1.4922	0.8607	9.90	0.53
II	99.9-127.9	16.65	1.4933	0.8609	34.33	1.85
III	127.9-150.4	25.25	1.4965	0.8646	52.06	2.81
Residue		1.3			2.68	0.14
Losses		0.5			1.03	0.06

TABLE 12

Dehydrogenation of the Paraffin-Naphthalene Part VT-2

Amt. of Fraction VT-2(g)	Amount of Fraction GT-2 obtained			Hydrogen and losses			
	actually (g)	corr. (g)	% in VT-2	% in TsT-2	(g)	% in VT-2	% in TsT-2
708.0	688.0	688.4	97.23	73.32	19.6	2.77	2.09

Separation of the catalyzate GT-2 into aromatic hydrocarbons and a mixture of paraffins and cyclopentanes. The catalyzate GT-2 was subjected to chromatographic adsorption analysis and was separated into aromatics DT-2 formed by the dehydrogenation of cyclohexane hydrocarbons, and the paraffin-cyclopentane fraction ET-2. The catalyzate GT-2, containing about 10% of aromatics (as shown by a separate test), was resolved with separation of an intermediate fraction and the subsequent resolution of that with the aid of isopentane. The results of the resolution of the catalyzate GT-2 are given in Table 13.

After removal of isopentane, the separated fractions, DT-2 and ET-2, had the following properties:

	n_{D}^{20}	d_4^{20}	Aniline point (°C)
DT-2	1.4953	0.8640	-
ET-2	1.3953	0.7028	66.1

Investigation of the aromatics DT-2. The aromatic hydrocarbons DT-2 were fractionated through a column of about 40-plate efficiency (similarly to the aromatics BT-2). The results of the fractionation, the properties of the fractions, and results of the optical analysis are given in Fig. 4 and Table 14. In the same table are given the results of the recalculation of the amounts of the separated aromatic fractions into the amounts of the corresponding cyclohexane hydrocarbons contained in the original gasoline.

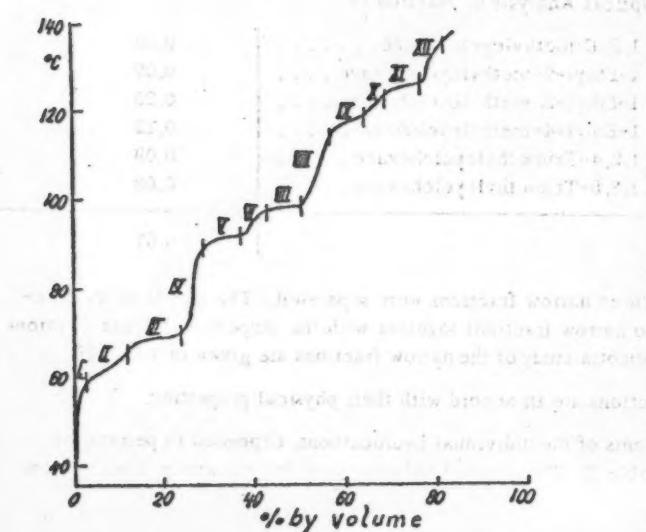


Fig. 5. Fractionation curve of the paraffin-cyclopentane part ET-2.

Investigation of the paraffin-cyclopentane part ET-2. The paraffin-cyclopentane part ET-2 was fractionated through a 50-plate column into narrow fractions. A preliminary determination of the fractionation curve was made with the same column on 100 ml of ET-2. The fractionation was carried out at a reflux number of 45-50 with continuous separation of distillate. The fractionation curve of ET-2 is given in Fig. 5. The vertical lines indicate the limits of the narrow fractions that were later taken; the selection of these limits was determined by the character of the fractionation curve and the boiling points of the individual hydrocarbons.

When the fractionation curve had been determined, 300 ml of ET-2 was fractionated into narrow fractions through the same column with continuous separation of

TABLE 13

Chromatographic Resolution of the Catalyzate GT-2

S-18 catalyzate with no reagent

Amt. of catalyzate GT-2 (g)	Results of separation											
	Aromatics DT-2				Paraffin-cyclopentane part ET-2				Losses			
	actual (g)	corr. (g)	% in GT-2	% in TsT-2	actual (g)	corr. (g)	% in GT-2	% in TsT-2	(g)	% in GT-2	% in TsT-2	
667.7	63.1	64.5	9.67	7.09	594.2	594.8	89.08	65.32	8.34	1.25	0.92	

TABLE 14

Fractionation of the Aromatics DT-2

Fraction No.	Boiling range in °C (760 mm)	Weight of fraction (g)	n_D^{20}	d_4^{20}	Content of fraction (% by weight in DT-2)	Content of corresponding cyclohexanes in TsT-2 (% by weight)
Amount taken for fractionation		62.75	1.4953	0.8640	100.00	
I	78.0-100.0	7.2	1.4953	0.8673	11.47	0.88
II	100.0-128.1	23.55	1.4941	0.8622	37.53	2.83
III	128.1-150.1	22.45	1.4954	0.8638	35.78	2.68
IV	150.1-162.9	5.25	1.4946	0.8657	8.37	0.62
Residue		1.55			2.47	0.18
Losses		2.75			4.38	0.33

Results of the Optical Analysis of Fraction III

Content of aromatic hydrocarbons in Fraction III (% by wt.)	Content of corresponding cyclohexane hydrocarbons in TsT-2 (% by wt.)	
o-Xylene	1.2-Dimethylcyclohexane	0.46
m-Xylene	1,3-Dimethylcyclohexane	1.10
p-Xylene	1,4-Dimethylcyclohexane	0.43
Ethylbenzene	Ethylcyclohexane	0.70
Total	100	2.69

Results of the Optical Analysis of Fraction IV

o-Xylene	5	1,2-Dimethylcyclohexane	0.03
1-Ethyl-2-methylbenzene	15	1-Ethyl-2-methylcyclohexane	0.09
1-Ethyl-3-methylbenzene	40	1-Ethyl-3-methylcyclohexane	0.25
1-Ethyl-4-methylbenzene	20	1-Ethyl-4-methylcyclohexane	0.12
1,2,4-Trimethylbenzene	15	1,2,4-Trimethylcyclohexane	0.09
1,3,5-Trimethylbenzene	5	1,3,5-Trimethylcyclohexane	0.03
Total	100		0.61

distillate, the reflux number being 40-45. In all, fifteen narrow fractions were separated. The results of the fractionation of the paraffin-cyclopentane part ET-2 into narrow fractions together with the properties of these fractions are given in Table 15, and the results of the Raman spectra study of the narrow fractions are given in Table 16.

The results of the optical analysis of these fractions are in accord with their physical properties.

All of the results obtained relating to the contents of the individual hydrocarbons, expressed in percent by weight on the whole gasoline TsT-2, are given in Table 2. The general balance sheet for the whole investigation is given in the same table.

TABLE 15

(Benzene), B.I. E.S.A.T.

Fractionation of the Paraffin-Cyclopentane Part ET-2

Fraction No.	Boiling range (°C)	Weight of fraction (g)	Content of fraction (% by wt.)		n _D ²⁰	d ₄ ²⁰	Aniline point (°C)
			in ET-2	in TsT-2			
Amt. taken for fractionation		211.4	100.00	65.32	1.3953	0.7028	66.1
I	33.9- 58.0	4.5	2.13	1.39	1.3689	0.6502	62.9
II	58.0- 65.0	19.3	9.13	5.96	1.3735	0.6580	71.4
III	65.0- 70.0	23.4	11.07	7.23	1.3772	0.6656	66.5
IV	70.0- 89.0	10.5	4.97	3.25	1.3963	0.7120	50.7
V	89.0- 92.5	21.4	10.12	6.61	1.3945	0.7037	63.5
VI	92.5- 98.0	8.0	3.78	2.47	1.3925	0.6977	65.1
VII	98.0- 99.0	17.2	8.14	5.32	1.3893	0.6874	67.8
VIII	99.0-115.5	15.5	7.33	4.79	1.4033	0.7233	61.8
IX	115.5-119.0	17.3	8.18	5.34	1.4018	0.7150	68.7
X	119.0-124.0	8.1	3.83	2.50	1.4045	0.7223	65.7
XI	124.0-126.0	14.1	6.67	4.36	1.4005	0.7113	69.0
XII	126.0-134.0	10.2	4.82	3.15	1.4044	0.7209	68.4
XIII	134.0-138.0	9.3	4.40	2.87	1.4145	0.7438	67.2
XIV	138.0-144.5	12.8	6.05	3.95	1.4128	0.7382	69.2
XV	144.5-149.6	7.8	3.69	2.41	1.4110	0.7336	70.5
Residue.....	7.0	3.31	2.16			
Losses.....	5.0	2.38	1.56			

TABLE 16

Results of the Optical Investigation of Narrow Fractions of the Paraffin-Cyclopentane Part ET-2

Hydrocarbons found by the optical method	Content of hydrocarbons (% by wt.)		Hydrocarbons found by the optical method	Content of hydrocarbons (% by wt.)	
	in the fraction	in TsT-2		in the fraction	in TsT-2
1	2	3	4	5	6
Fraction I			Fraction VI		
Pentane.....	60	0.83	3-Methylhexane	5	0.12
Cyclopentane.....	15	0.21	trans-1,2-Dimethylcyclopentane.....	15	0.37
2,2-Dimethylbutane.....	5	0.07	Heptane.....	80	1.98
2-Methylpentane.....	20	0.28	Fraction VII		
Fraction II			Heptane.....	100	5.32
2-Methylpentane.....	45	2.68	Fraction VIII		
3-Methylpentane.....	33	1.97	Heptane.....	51	2.44
Hexane.....	22	1.31	cis-1,2-Dimethylcyclopentane.....	10	0.48
Fraction III			Methylcyclohexane	19	0.91
Hexane.....	94	6.80	Ethylcyclopentane	15	0.72
3-Methylpentane.....	6	0.43	2-Methylheptane.....	5	0.24
Fraction IV			Fraction IX		
Hexane.....	10	0.32	2-Methylheptane	60	3.20
Methylcyclopentane.....	75	2.44	3-Methylheptane	25	1.34
Cyclohexane	10	0.33	4-Methylheptane	15	0.80
2-Methylhexane	5	0.16	Fraction X		
Fraction V			2-Methylheptane	50	1.25
2-Methylhexane	35	2.31	3-Methylheptane	15	0.37
3-Methylhexane	50	3.31	1,1-Dimethylcyclohexane	5	0.13
trans-1,2-Dimethylcyclopentane	15	0.99	Octane	30	0.75

TABLE 16 (Continued)

TABLE 16

1	2	3	4	5	6
Fraction XI			Not accounted for	45	1.29
Octane	94	4.10	Fraction XIV		
Not accounted for	6	0.26	1,1,3-Trimethylcyclohexane	~20	0.79
Fraction XII			4-Methyloctane	40	1.58
Octane	72	2.27	3-Methyloctane	30	1.18
1,1,3-Trimethylcyclohexane	28	0.88	Not accounted for	10	0.40
Fraction XIII			Fraction XV		
1,1,3-Trimethylcyclohexane	~35	1.01	Nonane	85	2.05
4-Methyloctane	20	0.57	Not accounted for	15	0.36

The laboratory assistants, T. V. Lapshina, V. A. Ovodova, K. G. Ryabova, and G. S. Taits, took part in this investigation.

SUMMARY

1. By the aid of the combination method of investigating the individual hydrocarbon composition of straight-run gasolines, the analysis has been carried out of a gasoline having an upper boiling limit of 150° derived from a sample of a low-sulfur Tuimazin petroleum (Devonian level).
2. The individual hydrocarbon composition of the Tuimazin gasoline has been accounted for quantitatively to the extent of 87.9% (by weight on the whole gasoline). The total losses were about 6%.
3. It has been found that normal paraffins predominate in this essentially paraffin gasoline from Tuimazin petroleum. Among the cyclopentanes, methylcyclopentane is present in the greatest amount. Among the cyclohexanes, methyl-, 1,3-dimethyl-, and 1,1,3-trimethyl-cyclohexanes are present in the greatest amounts. Among the aromatic hydrocarbons, toluene and m-xylene are present in the greatest amounts.

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* See Consultants Bureau Translation, page 215.

** " " " " 225.

COMPLEX COMPOUNDS OF METAL HALIDES WITH ALCOHOLS

A. B. Kuchkarev and N. I. Shuikin

In connection with some investigations that we are carrying out on the alkylation of aromatic compounds with alcohols in presence of $ZnCl_2$ and other metal chlorides, we have studied the reactions of metal halides ($ZnCl_2$, $ZnBr_2$, $AlCl_3$, $CdCl_2$, $MgCl_2$ and $CaCl_2$) with various alcohols (cyclohexanol, menthol, isopropyl alcohol, 2-methyl-2-butanol, and 1,1-dimethylethanol). Only a few papers have appeared that describe the preparation and properties of compounds of metal halides with various alcohols. These compounds have been regarded as analogs of the crystal hydrates of salts, and have therefore been termed crystal alcoholates [1].

The first compounds of this class were prepared as long ago as 1827. The compounds then obtained were those formed by $CaCl_2$ with methyl and ethyl alcohols. Later compounds containing other metals were described, for example, compounds of $CaCl_2$ [2], $MgCl_2$, $MgBr_2$, and $LiCl$ [3], $SrBr_2$ [4], and NaI [5].

Menshutkin [6] made a detailed study of the compounds formed by $MgBr_2$, MgI_2 , and $CaCl_2$ with various alcohols and ethers. He established that these compounds vary in composition according to the conditions under which the reaction is carried out: $CaCl_2$ gives a compound of the type $CaCl_2 \cdot 4ROH$ at below 55° , and of the type $CaCl_2 \cdot 3ROH$ at above this temperature. He studied also the compounds formed by phenol and by phenetole with $SbCl_3$, and isolated $2SbCl_3 \cdot C_6H_5OH$ and $SbCl_3 \cdot C_6H_5OC_2H_5$ [7]. Compounds of alcohols with boron trifluoride and aluminum chloride are also known. Boron trifluoride [8] will unite both with one and with two molecules of alcohol. According to the conditions, aluminum chloride [9] reacts with alcohols in two directions: in the cold crystalline addition products of the type $Al_2Cl_6 \cdot nROH$ are formed, and at higher temperatures with excess of $AlCl_3$ substitution products of the type $Al_2Cl_4(OR)_2$ are obtained.

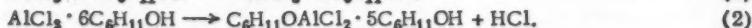
Tsukervanik [10] made a detailed study of the reaction of isobutyl alcohol with $AlCl_3$, and he obtained the crystalline partial alkoxide $AlCl_2O \cdot C_4H_9$; investigations on the compounds of $FeCl_3$ with alcohols [11] find their place here. Molecular compounds of alcohols with other metal chlorides are also described in the literature [12].

We have prepared a compound of cyclohexanol and zinc bromide by a method described previously [13]; it contains two molecules of cyclohexanol and one of zinc bromide, and is a crystalline substance, readily soluble in organic solvents. The benzene and acetone solutions of this substance have acidic properties; when it is heated with phenol, p-cyclohexylphenol is formed; with acetic acid it gives cyclohexyl acetate.

The compound of aluminum chloride and cyclohexanol was prepared by reaction in the cold between the component substances in petroleum ether (b.p. 48-50°) solution. The white crystalline substance $AlCl_3 \cdot 6C_6H_{11}OH$ was formed. This substance is very hygroscopic, and it dissolves in organic solvents. Its benzene, alcohol, and acetone solutions show acid reactions to indicators (Methyl orange, phenylazo-1-naphthylamine, Dimethyl Yellow).

A solution prepared from $AlCl_3 \cdot 6C_6H_{11}OH$ and cyclohexanol was found to be electrically conducting. For 0.02M $AlCl_3 \cdot 6C_6H_{11}OH$ in cyclohexanol $\lambda_m = 2.40$; and for 0.01M $\lambda_m = 1.20$ (20°). This compound is decomposed by heat with formation of cyclohexanol, cyclohexene, chlorocyclohexane, HCl , and other substances. Long heating of $AlCl_3 \cdot 6C_6H_{11}OH$ (water bath) in petroleum ether solution until evolution of HCl ceases leads to the formation of a crystalline substance corresponding in composition to $C_6H_{11}OAlCl_2 \cdot 5C_6H_{11}OH$. A solution of this substance in benzene has acidic properties. At 150-200° it decomposes to cyclohexanol, cyclohexene, chlorocyclohexene, and $AlCl_2OH$.

On the basis of the results described above and in the literature [14], the reaction of $AlCl_3$ with cyclohexanol may be represented by the following scheme:



Menthol and zinc chloride form the crystalline compound $C_{10}H_{19}OH \cdot ZnCl_2$. This is decomposed by heat

into menthene, $ZnCl_2$, and water. It is readily soluble in organic solvents.

In order to compare the complex compounds of zinc and aluminum halides with other analogous compounds, we have studied also the complexes formed by cadmium, calcium, and magnesium chlorides with various alcohols. At 130° calcium chloride and cyclohexanol form a white crystalline substance, corresponding in composition to the formula $CaCl_2 \cdot 3C_6H_{11}OH$. It is decomposed by heat into $CaCl_2$ and cyclohexanol, no cyclohexene formation being observed. An attempt to effect its condensation with phenol did not lead to the formation of *p*-cyclohexylphenol [distinction from $(C_6H_{11}OH)_2 \cdot ZnBr_2$]. This compound is difficultly soluble in organic solvents; its benzene solution gives a weakly acid reaction to phenylazo-1-naphthylamine.

With cyclohexanol and 2-methyl-2-butanol, magnesium chloride gives crystalline compounds having the compositions $MgCl_2 \cdot 3C_6H_{11}OH$ and $MgCl_2 \cdot 3C_5H_{11}OH$ (tert.). The second compound, when heated in a water bath with glacial acetic acid, reacts with formation of 1,1-dimethylpropyl acetate. When heated, both compounds decompose into $MgCl_2$ and the corresponding alcohol.

Cadmium chloride readily reacts with cyclohexanol and with isopropyl alcohol, the crystalline substances $CdCl_2 \cdot C_6H_{11}OH$ and $CdCl_2 \cdot C_3H_7OH$ -1 being formed. These are almost insoluble in organic solvents and do not have acidic properties. When heated, they decompose with formation of the corresponding alcohols and $CdCl_2$.

We then studied the reactions of 2-methyl-2-butanol and 1,1-dimethylethanol with $ZnCl_2$ and $ZnBr_2$. We isolated crystalline compounds consisting of two molecules of alcohol and one of zinc halide. These compounds are all very hygroscopic. They are readily soluble in organic solvents, and their solutions in benzene have acidic properties. When heated, they readily decompose with formation of olefins, the corresponding metal halides, and water. When the compound of $ZnBr_2$ with $C_6H_{11}OH$ (tert.) is heated with phenol, *p*-(1,1-dimethylpropyl) phenol is formed; with acetic acid, 1,1-dimethylpropyl acetate is formed.

On the basis of the facts given above we consider that the compounds formed by the metal halides studied with alcohols can be differentiated as follows, according to their behavior.

1. The compounds formed by $CaCl_2$, $MgCl_2$ and $CdCl_2$ with alcohols, unlike the analogous compounds of $ZnCl_2$, $ZnBr_2$ and $AlCl_3$ are decomposed by heat into the corresponding alcohols and metal halides. They are difficultly soluble in organic solvents, and their solutions have only very weakly acid properties ($CaCl_2$ compounds), or are completely devoid of such properties ($CdCl_2$ and $MgCl_2$ compounds). We consider that these compounds are typical crystal alcoholates.

2. The compounds formed by $ZnCl_2$, $ZnBr_2$ and $AlCl_3$ with alcohols are different in character. They have more strongly marked acid properties than compounds of the first group, and they have definite melting points. Also, at temperatures above their melting points they decompose with formation of new compounds (C_nH_{2n} , RX , ROH , H_2O and others). This indicates that the linkage between $ZnCl_2$, $ZnBr_2$, $AlCl_3$ and alcohols is stronger than in compounds formed by the metal halides of the first group (Cd, Ca, Mg). It is by this difference in the properties of the halogen compounds of Zn and Al on the one hand and of Ca, Mg, and Cd on the other that the behavior of metal halides in the alkylation reactions of alcohols with aromatic compounds can be explained.

On the basis of our results and of those described in the literature it must be supposed that the compositions of the complex compounds formed by metal halides with alcohols depend on the reaction conditions and the chemical nature of the metal halides. For example, for Zn halide compounds with two molecules of alcohol are characteristic; for Al those with six, for Cd those with one, and for Ca and Mg those with three.

Also, in order to determine whether complex-formation may occur between Zn halides and olefins, we have studied the action of 2-methyl-2-butene and hexene isomers (a mixture of 2,3-dimethyl-1-butene and 2,3-dimethyl-2-butene) on zinc bromide. It was found that zinc bromide reacts with these olefins in presence of moisture. Crystalline compounds of the following composition were obtained: $(C_5H_{10})_2 \cdot ZnBr_2 \cdot 2H_2O$ and $C_6H_{12} \cdot 2ZnBr_2 \cdot H_2O$.

These compounds are very hygroscopic, and they have acidic properties. They are decomposed by water into the corresponding alcohols and zinc bromide. With phenol, alkylphenols are formed. They enter into an esterification reaction with acetic acid with formation of esters. Kondakov [15], together with other complex compounds of zinc chloride, described for the first time the complex formed from 2-methyl-2-butene and zinc chloride, which had the composition $C_5H_{10} \cdot 2ZnCl_2 \cdot H_2O$. We have repeated Kondakov's experiments with 2-methyl-2-butene and zinc chloride, and we have succeeded in isolating this complex, which was found to have acidic properties and to enter into the esterification reaction with organic acids and the alkylation reaction with phenol.

EXPERIMENTAL

Starting Materials. Anhydrous metal halides were prepared from commercial products as indicated in the literature [15]. The alcohols were made absolute by a previously described method [13]. The reactions were carried out in a small round-bottomed flask fitted with reflux condenser protected by a calcium chloride tube.

Cyclohexanol and Zinc Bromide. A mixture of 30 g (0.3 mole) of cyclohexanol and 22.4 g (0.1 mole) of zinc bromide was heated in an oil bath for six hours. The reaction mixture was then treated with a mixture of petroleum ether and diethyl ether, when white needles were precipitated. They melted at 74-76° and were very hygroscopic; they dissolved readily in benzene, ether, acetone, and alcohol, but not readily in petroleum ether. A benzene solution of this substance gave an acid reaction with various indicators (phenylazo-1-naphthylamine, Methyl orange, Dimethyl Yellow). When the complex was heated at above 140°, it decomposed into cyclohexene, $ZnBr_2$, and water.

Found %: Br 37.83

$ZnBr_2 \cdot 2C_6H_{11}OH$. Calculated %: Br 37.64

Found: M 415 (cryoscopically in benzene solution)

$ZnBr_2 \cdot 2C_6H_{11}OH$. Calculated: M 425

Phenol and $ZnBr_2 \cdot 2C_6H_{11}OH$. A mixture of 14 g (0.15 mole) of phenol and 10.5 g (0.025 mole) of $ZnBr_2 \cdot 2C_6H_{11}OH$ was heated at 145-150° for four hours. The contents of the flask were then decomposed with cold acidified water. The organic part was separated, and the lower, aqueous layer was extracted twice with a small amount of benzene. The benzene extracts were united to the organic part, which was then washed, dried with $CaCl_2$, and fractionated, two fractions being obtained:

Fraction I, b.p. 180-240°: 9.3 g

Fraction II, b.p. 240-300°: 7.2 g

When Fraction II was allowed to stand, crystals of p-cyclohexylphenol separated. The liquid part of Fraction II, after removal of the crystals, was united with Fraction I, which was then treated with 15% NaOH solution. The alkaline solution was neutralized with dilute HCl, and the substance that then separated was washed, dried with $CaCl_2$, and fractionated. Altogether, 5.1 g (60%) of p-cyclohexylphenol was obtained; the by-products (phenol ethers) were not studied.

p-Cyclohexylphenol [16] was obtained as white crystals, m.p. 128-129° (from benzene).

Found %: C 81.82; H 9.42

$C_{12}H_{16}O$. Calculated %: C 81.76; H 9.16

Acetic Acid and $ZnBr_2 \cdot 2C_6H_{11}OH$. A mixture of 4 g (0.06 mole) of CH_3COOH and 8.5 g (0.02 mole) of $ZnBr_2 \cdot 2C_6H_{11}OH$, was heated at 100-120° for ten hours. Suitable treatment and fractionation of the reaction product yielded 2.5 g (44%) of cyclohexyl acetate, a liquid of b.p. 172-174°; d_{20}^{20} 0.9685; n_D^{20} 1.4430; found MR 38.58; calculated at $C_8H_{14}O_2$ MR 38.60.

Reaction Product from Cyclohexanol and Aluminum Chloride. The substances taken were cyclohexanol (20 g, i.e. 0.2 mole), aluminum chloride, (2.5 g, i.e. 0.016 mole), and petroleum ether (15 ml). The reaction was carried out in the cold with vigorous stirring. The aluminum chloride was added slowly (over a period of ten hours) to a solution of the cyclohexanol in the petroleum ether. During the reaction no evolution of hydrogen chloride was to be noted. When reaction was complete, the mass was left overnight. White crystals came down, and these were filtered off, washed with petroleum ether (b.p. 45-50°), pressed off, and dried in nitrogen in a desiccator over P_2O_5 . The total amount of product obtained was 12 g (84%). The complex obtained melted at 60-65° with decomposition, and was soluble in benzene, alcohol, acetone, and ether, but difficultly soluble in petroleum ether; its benzene solution gave an acid reaction to various indicators (Methyl orange, phenylazo-1-naphthylamine). Analysis for carbon, hydrogen, aluminum, and chlorine indicated the formation of a compound of the composition $AlCl_3 \cdot 6C_6H_{11}OH$.

Found %: C 58.43; H 9.51; Cl 14.35; Al 3.48

$AlCl_3 \cdot 6C_6H_{11}OH$. Calculated %: C 58.91; H 9.81; Cl 14.50; Al 3.67

When $AlCl_3 \cdot 6C_6H_{11}OH$ was heated to 150-200°, it decomposed with formation of cyclohexene, chlorocyclohexane, cyclohexanol, and hydrogen chloride. When a petroleum ether solution of $AlCl_3 \cdot 6C_6H_{11}OH$ was heated in a water bath under reflux until, after a considerable time, the evolution of HCl ceased, a crystalline

substance melting with decomposition at 50-55° was formed. On the basis of analysis for chlorine and aluminum it may be supposed that this substance had the composition $\text{AlCl}_2\text{OC}_6\text{H}_{11} \cdot 5\text{C}_6\text{H}_{11}\text{OH}$.

Found %: Al 3.97; Cl 10.44

$\text{AlCl}_2\text{OC}_6\text{H}_{11} \cdot 5\text{C}_6\text{H}_{12}\text{O}$. Calculated %: Al 3.87; Cl 10.17

When $\text{AlCl}_2\text{OC}_6\text{H}_{11} \cdot 5\text{C}_6\text{H}_{12}\text{O}$ was heated at above 150°, cyclohexene, chlorocyclohexane, and cyclohexanol were obtained.

Cyclohexanol and Magnesium Chloride. A mixture of 25 g (0.25 mole) of cyclohexanol and 4.7 g (0.05 mole) of magnesium chloride was heated for ten hours at 125-130°. The product was then filtered off, washed with petroleum ether, and dried in a desiccator over P_2O_5 . The substance so obtained consisted of extremely hygroscopic white crystals, which, when heated, decomposed into the original components without melting. The substance was of low solubility in organic solvents (benzene and acetone), apart from alcohol, in which it dissolved readily. Its benzene and acetone solutions gave almost no signs of acid reaction with phenylazo-1-naphthylamine. When heated (water bath) with glacial acetic acid, cyclohexyl acetate was formed. According to analysis the compound had the composition $\text{MgCl}_2 \cdot 3\text{C}_6\text{H}_{11}\text{OH}$.

Found %: Cl 17.40; Mg 6.50

$\text{MgCl}_2 \cdot 3\text{C}_6\text{H}_{12}\text{O}$. Calculated %: Cl 17.72; Mg 6.15.

2-Methyl-2-butanol and Magnesium Chloride. A mixture of 9 g (0.1 mole) of 2-methyl-2-butanol and 1.2 g (0.05 mole) of magnesium chloride was heated at 100-110° for six hours. The resulting crystalline substance (white needles) was filtered off, washed with petroleum ether, and dried in a desiccator over P_2O_5 . It was found to be of low solubility in benzene, ether, and acetone, but readily soluble in alcohol. When heated, it decomposed without melting into magnesium chloride and the original alcohol. It had no acidic properties. When it was heated with phenol at 140°, no (1,1-dimethylpropyl) phenol was formed.

Found %: Cl 20.17

$\text{MgCl}_2 \cdot 3\text{C}_6\text{H}_{11}\text{OH}$. Calculated %: Cl 19.77

Cyclohexanol and Calcium Chloride. A mixture of 30 g (0.3 mole) of cyclohexanol and 5.5 g (0.05 mole) of calcium chloride was heated at 120-130° for six hours. After suitable treatment the resulting white crystals were dried over P_2O_5 in a desiccator. This substance was found to be soluble in alcohol and acetone, but difficultly soluble in benzene and petroleum ether. Its benzene solution gave a very feeble acid reaction to phenylazo-1-naphthylamine. When heated, it decomposed into CaCl_2 and the original cyclohexanol. The compound obtained had the composition $\text{CaCl}_2 \cdot 3\text{C}_6\text{H}_{11}\text{OH}$.

Found %: C 52.00; H 9.35; Cl 16.88; Ca 9.80

$\text{CaCl}_2 \cdot 3\text{C}_6\text{H}_{12}\text{O}$. Calculated %: C 52.55; H 8.75; Cl 17.0; Ca 9.75

Cyclohexanol and Cadmium Chloride. A mixture of 20 g (0.3 mole) of cyclohexanol and 5.6 g (0.05 mole) of cadmium chloride was heated at 125-130° for eight hours. The white crystalline substance obtained was very hygroscopic and was difficultly soluble in benzene, acetone, and petroleum ether; it readily dissolved in alcohol. The substance was found to have very feeble acidic properties. When heated, it decomposed into CdCl_2 and the original cyclohexanol.

Found %: C 25.46; 25.47; H 4.06; 4.05; Cl 25.49; 25.28

$\text{CdCl}_2 \cdot \text{C}_6\text{H}_{12}\text{O}$. Calculated %: C 25.40; H 4.24; Cl 25.03

Isopropyl Alcohol and Cadmium Chloride. A mixture of 12 g (0.2 mole) of isopropyl alcohol and 9 g (0.1 mole) of cadmium chloride was heated at 110-120° for five hours. A crystalline substance was formed and was found to be of low solubility in many organic solvents (benzene, toluene, acetone, and ether), but readily soluble in alcohols. When heated, this substance decomposed without melting into CdCl_2 and the original isopropyl alcohol.

Found %: Cl 28.80

$\text{CdCl}_2 \cdot \text{C}_3\text{H}_7\text{OH}$. Calculated %: Cl 29.00

(-)-Menthol and Zinc Chloride. A mixture of 7.1 g (0.05 mole) of menthol and 3.0 g (0.022 mole) of zinc chloride was heated at 100-110° for eight hours. The resulting white needles were soluble in many organic solvents (benzene, alcohol, acetone, ether), but difficultly soluble in petroleum ether. A benzene solution of the substance was found to have acid properties. It melted with decomposition at 103-105°.

5.6 g. obtained after heating for 25 days. Found %: Cl 24.66
 $ZnCl_2 \cdot C_{10}H_{19}OH$. Calculated %: Cl 24.42

1,1-Dimethylethanol and Zinc Chloride. A mixture of 15 g (0.2 mole) of 1,1-dimethylethanol and 6.8 g (0.05 mole) of zinc chloride was sealed in a glass tube and set aside at room temperature for 25 days. White crystals (prisms) formed in the reaction mixture, and were filtered off, washed with petroleum ether, and dried over P_2O_5 . The resulting crystals were very hygroscopic and readily became liquid when exposed to the atmosphere. They were readily soluble in benzene, ether, acetone, and alcohols, but difficultly soluble in petroleum ether, pentane, and hexane. The benzene solution of this complex had acidic properties. The melting point of the substance was 56-58°.

Found %: Cl 24.92
 $ZnCl_2 \cdot 2C_4H_9O$. Calculated %: Cl 25.00

Found: M 278.7
 $ZnCl_2 \cdot 2C_4H_9O$. Calculated: M 284.4

When the substance was heated (water bath) with glacial acetic acid, tert-butyl acetate was formed.

Alkylation of Phenol by the Complex $ZnCl_2 \cdot 2C_4H_9OH$ (Tert). A mixture of 2.84 g (0.01 mole) of $ZnCl_2 \cdot 2C_4H_9OH$ and 9.4 g (0.1 mole) of phenol was heated in a water bath for six hours. Suitable treatment of the reaction product yielded 15 g of p-tert-butylphenol (m.p. 98-99°).

Found %: C 79.81; H 9.12
 $C_{10}H_{14}O$. Calculated %: C 80.00; H 9.33

2-Methyl-2-butanol and Zinc Chloride. A mixture of 22 g (0.25 mole) 2-methyl-2-butanol and 13.6 g (0.1 mole) zinc chloride was stored in a sealed tube for 45 days*. When white crystals (prisms) had appeared. These were filtered off, washed with petroleum ether, and dried over P_2O_5 . The substance so obtained, which melted at 62-64°, was very hygroscopic and of good solubility in organic solvents. Its benzene solutions had acidic properties. With glacial acetic acid it yielded 1,1-dimethylpropyl acetate.

Found %: Cl 22.45
 $ZnCl_2 \cdot 2C_5H_{12}O$. Calculated %: Cl 22.74
Found: M 304
 $ZnCl_2 \cdot 2C_5H_{12}O$. Calculated: M 312

Alkylation of Phenol by the Complex $ZnCl_2 \cdot 2C_5H_{11}OH$ (tert). A mixture of 3 g (0.01 mole) of $ZnCl_2 \cdot 2C_5H_{11}OH$ and 9.4 g (0.1 mole) of C_6H_5OH was heated in a water bath for six hours. The product was 1.5 g of p-(1,1-dimethylpropyl)phenol, m.p. 91-92°.

2-Methyl-2-butanol and Zinc Bromide. Reaction between 22 g (0.25 mole) of 2-methyl-2-butanol and 11.25 g (0.05 mole) of zinc bromide yielded a crystalline substance (prisms) which readily became liquid when exposed to the atmosphere. The crystals were readily soluble in many organic solvents, but difficultly soluble in petroleum ether; they melted at 60-62°. When heated with acetic acid, they yielded 1,1-dimethylpropyl acetate, and when heated with phenol they gave p-(1,1-dimethylpropyl)phenol.

Found %: Br 40.24; 39.86
 $ZnBr_2 \cdot 2C_5H_{12}O$. Calculated %: Br 40.00
Found: M 393.6
 $ZnBr_2 \cdot 2C_5H_{12}O$. Calculated: M 401.2

1,1-Dimethylethanol and Zinc Bromide. Reaction between 15 g (0.2 mole) of 1,1-dimethylethanol and 11.25 g (0.05 mole) of zinc bromide yielded prisms of m.p. 53-55°. They were readily soluble in benzene, toluene, and alcohol, but of poor solubility in hydrocarbons of the aliphatic series. Water decomposed them with formation of the alcohol (C_4H_9OH). The benzene solutions of the substance were found to have acidic properties. The complex was found to take part in esterification reactions with organic acids (CH_3COOH).

Found %: Br 42.15
 $ZnBr_2 \cdot 2C_4H_9O$. Calculated %: Br 42.87

2-Methyl-2-butene and Zinc Bromide. A mixture of 7 g (0.1 mole) of 2-methyl-2-butene and 24 g of moist zinc bromide was set aside in a sealed tube for a long period of time (ten months). The tube was then

* At room temperature.

opened, and the white crystals that had formed (needles, m.p. 60-62°) were filtered off, washed with pentane, and dried over P_2O_5 in a vacuum desiccator. The resulting substance was very hygroscopic; it was readily soluble in many organic solvents, but difficultly soluble in hydrocarbons (pentane, hexane, petroleum ether). Its benzene solutions gave an acid reaction to phenylazo-1-naphthylamine. When treated with water, the substance was decomposed into 2-methyl-2-butanol and zinc bromide. When a mixture of it with phenol was heated (water bath) (1,1-dimethylpropyl) phenol was formed. With acetic acid under the same conditions it yielded 1,1-dimethylpropyl acetate. Analyses of this substance indicated the composition $(C_5H_{10})_2 \cdot ZnBr_2 \cdot 2H_2O$.

Found %: C 29.11; 28.93; H 6.04; 5.91; Br 40.25; 40.15
 $(C_5H_{10})_2 \cdot ZnBr_2 \cdot 2H_2O$. Calculated %: C 29.92; H 5.95; Br 39.91

Hexene Isomers and Zinc Bromide. A mixture of 24 g of $ZnBr_2$ and 7 g of a moist mixture of 2,3-dimethyl-1-butene and 2,3-dimethyl-2-butene was set aside in a sealed tube at room temperature for six months. The crystals (prisms) that had formed in the course of this time were separated from liquid, washed, and dried in a desiccator over P_2O_5 . The resulting crystals were very hygroscopic, were readily soluble in benzene, alcohol and acetone, and had acidic properties. Water decomposed the complex with formation of 2,3-dimethyl-2-butanol. Analyses indicated that the compound had the formula $C_6H_{12} \cdot 2ZnBr_2 \cdot H_2O$.

Found %: C 13.21; H 2.71; Br 58.07
 $C_6H_{12} \cdot 2ZnBr_2 \cdot H_2O$. Calculated %: C 13.04; H 2.53; Br 57.86

SUMMARY

1. It has been shown that, when the halides of certain metals of the second and third groups of Mendeleev's system ($ZnCl_2$, $ZnBr_2$, $AlCl_3$, $CaCl_2$, $MgCl_2$ and $CdCl_2$) react with aliphatic (isopropyl alcohol, 1,1-dimethyl-ethanol, 2-methyl-2-butanol) and cyclic (cyclohexanol, menthol) alcohols, crystalline complex compounds of an acidic nature are formed. In this reaction, zinc halides unite with two alcohol molecules, aluminum halides with six, calcium and magnesium with three, and cadmium with one.
2. When heated, the complexes formed with $ZnCl_2$, $ZnBr_2$, and $AlCl_3$, unlike those formed with $MgCl_2$, $CaCl_2$, and $CdCl_2$, break down with formation of new substances (C_nH_{2n} , RX, ROH, MeX_2 , H_2O , etc.). The compounds of $MgCl_2$, $CdCl_2$, and $CaCl_2$ with alcohols decompose into the original components under these conditions.
3. When these metal halide complexes are treated with organic acids (CH_3COOH and others), esters are formed.
4. In presence of moisture 2-methyl-2-butene, 2,3-dimethyl-1-butene, and 2,3-dimethyl-2-butene react with zinc bromide with formation of crystalline compounds of composition $(C_5H_{10})_2 \cdot ZnBr_2 \cdot 2H_2O$ and $C_6H_{12} \cdot 2ZnBr_2 \cdot H_2O$.

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REACTIONS OF CYCLOHEXENE AT ALUMINOSILICATE CATALYSTS OF DIFFERENT ALUMINA AND SILICA CONTENTS UNDER CONDITIONS PRECLUDING CRACKING.

SELECTIVE POISONING BY SODIUM IONS

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In this paper we describe preliminary results of a study of the mechanism of the catalytic action of aluminosilicates on the polymerization and "skeleton" isomerization of hydrocarbons. We were interested in the question of whether polymerization and skeleton isomerization proceeds at the "acidic" active centers associated with cracking and hydrogen redistribution,* or at the active centers of the aluminum oxide.

In the solution of this question we were guided by the following considerations. The relation between the catalytic activity of aluminosilicates and their composition (the ratio $\text{Al}_2\text{O}_3:\text{SiO}_2$) is described for cracking and hydrogen redistribution by a curve having a maximum at 30% by weight of Al_2O_3 and 70% by weight of SiO_2 [1-7]. An analogous relationship is known between the acidity of aluminosilicates and the $\text{Al}_2\text{O}_3:\text{SiO}_2$ ratio [6, 8]. "Acidic" active centers are poisoned (cracking) as a result of the exchange adsorption of sodium ions [7, 9]. These facts are to be explained on the basis of the relationship between the catalytic activity of aluminosilicates and their chemical properties, particularly acidity, and the cracking and hydrogen-redistribution centers are to be regarded as equivalent to an aluminosilicic acid, the hydrogen of which participates in the transfer of hydrocarbon hydrogen during the catalytic reaction [7].

For any reaction that is accelerated by aluminosilicates, a study of the dependence of its rate on the $\text{Al}_2\text{O}_3:\text{SiO}_2$ ratio in the catalyst and on the sodium ion concentration on the catalyst surface permits an approach to be made to the solution of the question of the nature of the active centers in this reaction. We have, therefore, studied polymerization and skeleton isomerization in presence of 1) aluminosilicates of different alumina and silica contents, and 2) aluminosilicates poisoned with respect to cracking and hydrogen redistribution by sodium ions.

As a subject for investigation we selected cyclohexene, which, at temperatures below that at which cracking begins, undergoes polymerization, skeleton isomerization, and hydrogen redistribution. The last reaction has been studied previously only in the case of unsaturated cracking gasoline [1]. We hoped to obtain some supplementary results on this reaction. In previous papers descriptions have been given of the method of preparation [1] and the adsorption properties [2, 5, 10] of the investigated catalysts, and also of the kinetics of the transformations of various hydrocarbons [1, 2, 3, 5, 11] in the presence of these catalysts.

Already in 1950 we established that treatment of an aluminosilicate catalyst with a solution of sodium chloride or carbonate selectively poisons the active centers; whereas activity for the cracking of cumene falls sharply, activity for the dehydration of ethanol is preserved. Adsorption of sodium ions does not appreciably affect the specific surface or the pore distribution [9]. We have established also that aluminum oxide that is active for dehydration does not adsorb Na ions from aqueous salt solutions and does not alter in catalytic activity for dehydration after treatment with a solution of sodium acetate.

Zelinsky and Arbuzov [12] investigated the transformations of cyclohexene at 400° in presence of aluminum oxide containing some silica gel, and they showed that the hydrogenated monomer fraction of the catalyzate consisted of methylcyclopentane. Nikolaeva, Tatevsky, and Frost [13] found that the monomer fraction of the transformation products of cyclohexene, which was passed over natural aluminosilicate at 260°, consisted of saturated and unsaturated hydrocarbons (methylcyclopentane, cyclohexane, methylcyclopentene, and cyclohexene). Petrov and Shchekin [14, 15] investigated the same reaction at 260° and 316° in presence of synthetic aluminosilicate and, while confirming the results of the previous investigators, showed that the polymer fraction consisted mainly of bicyclic hydrocarbons having one five- and one six-membered ring. The authors pointed out the absence of benzene among the light products and of cyclic hydrocarbons having two six- or two five-membered rings among the polymeric products. They suggested that isomerization in presence of aluminosilicates proceeds via depolymerization of an isomerized polymer of cyclohexene.

* Saturation of unsaturated hydrocarbons by redistribution of hydrogen.

EXPERIMENTAL

Cyclohexene, which was prepared by the dehydration of cyclohexanol (b.p. 158.5-159° (760 mm)) over phosphoric acid, had the following constants after being dried and then distilled through a 20-plate column: b.p. 82.5-83° (760 mm); n_D^{20} 1.4466; d_4^{20} 0.8090; iodine number 307.

The reaction was carried out at 350° (no cracking occurs at this temperature) in a continuous-flow apparatus. The monomer fraction (up to 85°) was distilled off from the catalyzate through a 10-plate column. The extent to which polymerization of cyclohexene occurred was determined from the yield of residue after the removal of the monomer fraction. The extent of hydrogen redistribution was determined from the iodine number of the monomer fraction. In order to determine the composition of the monomer fraction, one-half of it was treated with sulfuric acid (sp.gr. 1.84) to remove unsaturated hydrocarbons, and the other half was hydrogenated. The contents of methylcyclopentane and cyclohexane were determined separately for the hydrogenated and sulfonated parts by a refractive index method.* From the results obtained, the contents of methylcyclopentane, methylcyclopentene, cyclohexane, and cyclohexene in the monomer fraction were calculated. From the total content of five-membered hydrocarbons in the monomer fraction, the extent of the isomerization of cyclohexene was calculated. The method is accurate within 2-3%, calculated on the monomer fraction, and it has been verified by the analysis of artificial mixtures.

In Table 1 we give the results of experiments on the transformations of cyclohexene in presence of catalysts of different alumina and silica contents. The total degree of conversion was determined from the amount of unchanged cyclohexene.

TABLE 1

Temperature 350°; space velocity $v = 1.2$ liter/liter·hr; duration of experiment, 1 hour.

Composition of catalyst (% by wt. $\text{Al}_2\text{O}_3:\text{SiO}_2$)	Composition of catalyst (% by weight)		Composition of monomer fraction (% by weight on monomer fraction)				Total degree of conversion (%)
	polymers	monomers	saturated	unsaturated	5-membered	6-membered	
0:100	0	100	0	100	0	100	0
10:90	21	79	10	90	19	81	36
16:84	23	77	12	88	35	65	51
30:70	36	64	41.5	58.5	36	64	57
50:50	33	67	40	60	40	60	61
72:28	30	70	20	80	48	52	62
100:0	0	100	0	100	48	52	48

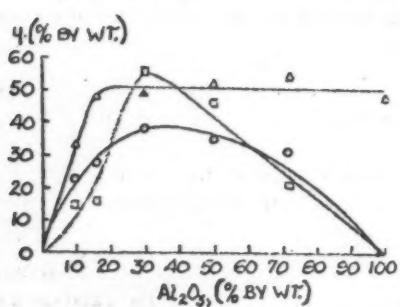


Fig. 1. Dependence of the conversion of cyclohexene on the composition of the aluminosilicate (recalculated to equal weights of samples): Δ = isomerization; \circ = polymerization; \square = hydrogen redistribution.

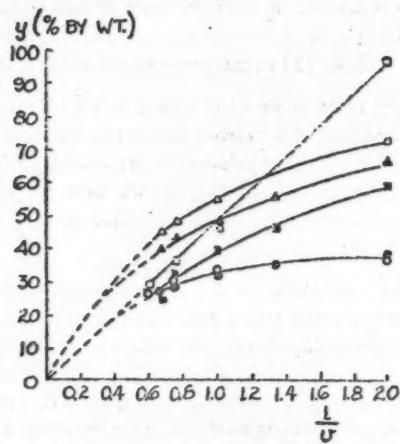


Fig. 2. Dependence of the conversion of cyclohexene on the reciprocal of the space velocity: original sample Δ = isomerization; \circ = polymerization; \square = hydrogen redistribution; sample containing 29 mg-equiv. of Na per 100 g \blacktriangle = isomerization; \bullet = polymerization; \blacksquare = hydrogen redistribution.

* Method used by the Kinetics and Catalysis Laboratory of the Petroleum Institute of the USSR Academy of Sciences.

It follows from Table 1 that polymerization and hydrogen redistribution proceed most rapidly in presence of a 30:70 catalyst. For these reactions the variation of activity with change in the composition of the catalyst repeats the results obtained previously for cracking and hydrogen redistribution in gasoline [1-5]. It would appear that the polymerization of cyclohexene proceeds at the same active centers in the aluminosilicate as those at which cracking and hydrogen redistribution occur. Isomerization proceeds differently: the activity of the catalyst for this reaction increases with increase in the alumina content of the catalyst. Pure aluminum oxide is active only for isomerization. The latter was checked at several space velocities (0.5; 0.66; 0.9; 1.2; 1.38; 2.0 liter/liter hr.).

The results given in Table 1 refer to equal apparent bulk volumes of the catalysts, which have different weights, since the bulk specific gravity depends on the $\text{Al}_2\text{O}_3:\text{SiO}_2$ ratio of the catalyst. In Table 2 and Fig. 1 we give the results of the same experiments after recalculation to equal amounts by weight of the catalysts. The recalculation was made on the basis of kinetic data (the change in yield of the particular substance resulting from change from equal volumes to equal weights was determined from the experimental kinetic curves). This recalculation did not affect the nature of the dependence of the activity of catalysts for polymerization and hydrogen redistribution on the $\text{Al}_2\text{O}_3:\text{SiO}_2$ ratio, as established from the results in Table 1.

In Table 3 we give the results of the study of the kinetics of the transformation of cyclohexene at a 50:50 aluminosilicate catalyst, pure (the "original"), and poisoned with sodium ions.

TABLE 2

Composition of catalyst (% by wt, $\text{Al}_2\text{O}_3:\text{SiO}_2$)	Apparent bulk sp.gr.	Space velocity corresponding to equal weights (liter/liter·hour)	Activity (% by weight)				total degree of conversion
			for polymerization •	for hydrogen redistribution **	for polymerization **		
0:100	0.36	0.65	0	0	0	0	0
10:90	0.44	0.78	23	15	33	55	
16:84	0.48	0.86	28	16	48	71	
30:70	0.49	0.80	38	56	49	77	
50:50	0.57	1.02	35	48	52	71	
72:28	0.61	1.11	31	24	54	67	
100:0	0.67	1.20	0	0	48	48	

• On catalyzate

** On monomer fraction

TABLE 3

Temperature 350°; duration of experiment, 1 hour; 50:50 catalyst, original and containing 29 mg-equiv Na per 100 g

v	1/v	Polymerization*		Hydrogen redistribution**		Isomerization***	
		original catalyst	poisoned catalyst	original catalyst	poisoned catalyst	original catalyst	poisoned catalyst
0.5	2	37	38	97	59	73	67
0.75	1.34	—	35	—	46	—	57
1.0	1.0	33	32	46	39	55	48
1.33	0.75	30	28	36	32	48	43
1.50	0.67	—	26	—	25	45	40
1.66	0.60	27	—	29	—	—	—

* Polymers in catalyzate (%)

** Saturated hydrocarbons in monomer fraction (%)

*** Five-membered hydrocarbons in monomer fraction (%)

The original catalyst (5-6 g) was saturated at room temperature with sodium ions by treatment with 60 ml portions of N sodium acetate for 1-2 days (Miesserov's method [16]).

The amount of adsorbed sodium ions was regarded as equivalent to the acid passing into the solution as a result of the exchange of the acidic hydrogen of the aluminosilicate structure for sodium ions. The acid so formed was determined by titration of the acetate solution with 0.02 N sodium hydroxide to phenolphthalein. It had been previously established that the sodium ion of sodium acetate solution does not replace the hydrogen of the hydroxyl groups of silica gel and alumina gel. The hydrogen ions of the "aluminosilicate" centers were, therefore, removed selectively from the surface. A sample containing 29 mg-equivalents of sodium per 100 g was obtained.

In Fig. 2 the results in Table 3 are presented in the coordinates: degree of conversion (%) and $\frac{1}{v}$ (the value of $\frac{1}{v}$ is proportional to the time of contact).

Polymerization and isomerization on the original and poisoned samples and redistribution on the poisoned sample are described by the equation:

$$v \ln \frac{1}{1-y} = \alpha + \beta vy \quad (1)$$

which was derived by Frost [17] for unimolecular reactions retarded by the reaction products and occurring in a continuous-flow system. In this equation y is the degree of conversion, α is a constant proportional to the rate constant, v is the space velocity; and β is the retardation constant.

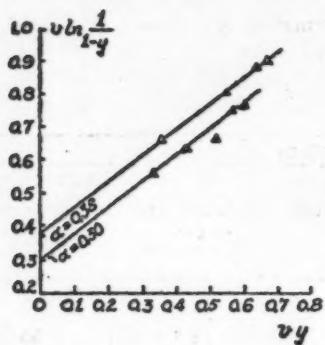


Fig. 3. Kinetics of the isomerization of cyclohexene: Δ = sample containing 29 mg-equiv. Na per 100 g; Δ = original sample.

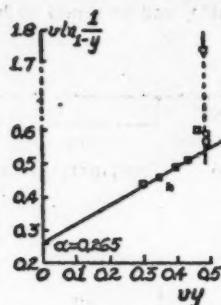


Fig. 4. Kinetics of hydrogen redistribution in the conversion of cyclohexene: \square = original sample; \blacksquare = sample containing 29 mg-equiv. Na per 100 g.

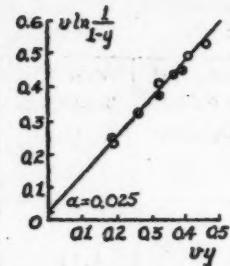


Fig. 5. Kinetics of the polymerization of cyclohexene: \circ = original sample; \bullet = sample containing 29 mg-equiv. Na per 100 g.

Figures 3, 4, and 5 present the results of a calculation by Frost's equation for the original and poisoned samples. In the calculation, in place of "y" in the equation, the figures in Table 3 have been substituted.

DISCUSSION OF RESULTS

A comparison of the results obtained for the original and poisoned samples shows that the sodium ion, exchange-adsorbed on the catalyst, very greatly reduces its activity for the redistribution of hydrogen. The activity for isomerization is also reduced, but not so greatly as for hydrogen redistribution. The activity for polymerization is identical, within the limits of experimental error, for the original sample and for the sample containing sodium. The value of α , which is proportional to the rate constant, fell as a result of the poisoning from 0.48 to 0.26 for redistribution, and from 0.37 to 0.27 for isomerization. It is noteworthy that the hydrogen-redistribution reaction, which before the poisoning is described by an equation of zero order ($vy = \text{const}$), is described after the poisoning by the equation for a unimolecular reaction retarded by the reaction products (Figs. 2 and 4, and Equation 1).

The results obtained on the redistribution of hydrogen during the transformations of cyclohexene confirm those obtained earlier on the same reaction: 1) the reaction is accelerated only by aluminosilicates, the original oxides, Al_2O_3 and SiO_2 being inactive; and 2) the most active catalyst is that having the ratio of 30:70 [1]. It has been shown for the first time that sodium adsorbed on aluminosilicate poisons it for hydrogen redistribution. These results, taken as a whole, confirm that hydrogen redistribution proceeds at the same "acidic aluminosilicate centers" as cracking does [3, 18].

Isomerization, which is accelerated by pure aluminum oxide, is appreciably retarded by the adsorption of sodium ions on the aluminosilicate. According to our results, pure aluminum oxide does not exchange-adsorb sodium ions from aqueous sodium acetate solutions and so cannot be poisoned for isomerization after treatment with this solution. The poisoning effect of the adsorption of sodium ions with respect to isomerization in presence of aluminosilicate indicates, in our opinion, that isomerizing power is possessed not only by the free aluminum oxide

existing in the catalyst, but also by those active aluminosilicate centers that promote cracking and hydrogen redistribution. This inference is in accord with the results that we have obtained for the dehydration of ethanol. For this reaction only aluminum oxide is active, and aluminosilicate does not alter in dehydration activity after treatment with aqueous sodium acetate. It is possible that isomerization at aluminosilicate active centers proceeds via the depolymerization of the isomerized polymer.

The results that we have obtained on polymerization do not resolve the question of whether this reaction proceeds at "acidic" centers, since, on the one hand, the dependence of activity on the composition of the catalyst is described for polymerization by a curve that is characteristic for catalysis at "acidic" aluminosilicate active centers, whereas, on the other hand, no appreciable poisoning of the catalyst with respect to polymerization was observed when 29 mg-equivalents of sodium per 100 g of catalyst was adsorbed. Further investigation of this reaction is now proceeding.

SUMMARY

1. A study has been made of the kinetics of the simultaneous reactions of polymerization, hydrogen redistribution, and isomerization under conditions precluding cracking, and it has been shown that the transformations of cyclohexene proceed at active centers of two types.
2. Hydrogen redistribution proceeds only at "acidic" aluminosilicate active centers. Isomerization proceeds at "acidic" active centers and on aluminum oxide.
3. Adsorption of sodium ions poisons aluminosilicate with respect to hydrogen redistribution and isomerization.

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reactions, which are being developed at present, are associated with the formation of new functional groups and the introduction of new radicals into the molecule. The first reaction is the copolymerization of methyl methacrylate with alkyl vinyl ethers, which is the subject of the present paper.

CHEMICAL REACTIONS OF UNSATURATED AND MACROMOLECULAR COMPOUNDS

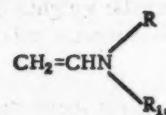
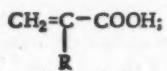
COMMUNICATION 2. COPOLYMERIZATION OF METHYL METHACRYLATE WITH ALKYL VINYL ETHERS

M. F. Shostakovskiy and A. M. Khomutov

The development of investigations on polymerization and copolymerization has been characterized until recently by the utilization of the double bonds of various unsaturated compounds as the basis of the synthetic potentialities of these reactions.

New synthetic potentialities for polymerization and copolymerization reactions are now emerging as a result of the application in these reactions of new compounds having not only multiple bonds, but also active functional groups, i.e., other reaction centers that may be utilized in the processes that we are considering.

As examples of new compounds that we have applied in polymerization and copolymerization reactions, we will cite the following:

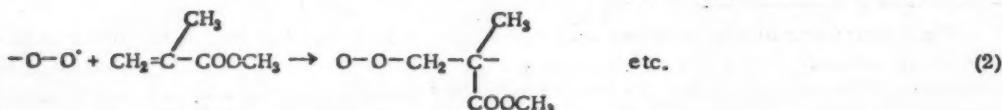
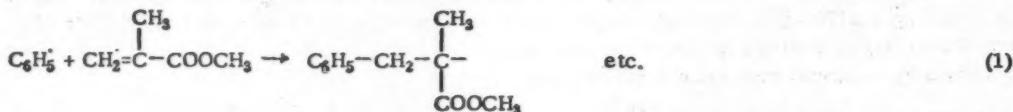


(R and R₁ may be Alk, Ar, aralkyl, or other radicals, which may contain substituents).

In our previous work [1] we have studied the behavior of methacrylic acid in copolymerization reactions with vinyl ethers. It was shown that, apart from the main copolymerization process, there were a number of simultaneous reactions associated with double bonds and functional groups containing mobile hydrogen. The presence in the molecules of several functional groups has a marked effect on the course of the polymerization of the original monomers, as compared, for example, with the polymerization of unsaturated compounds not containing active functional groups [2].

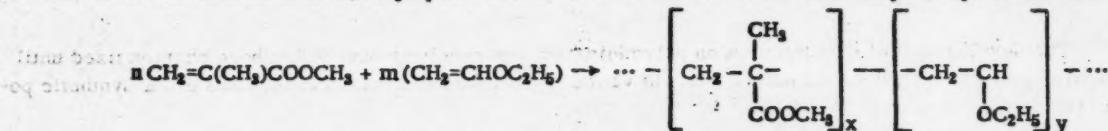
It was pointed out at the same time that alkyl vinyl ethers, which do not polymerize in presence of benzoyl peroxide [3] or oxygen [4], will copolymerize with methacrylic acid. It was of interest to establish the possibility of copolymerization between alkyl vinyl ethers and a methacrylic ester, in which the mobile hydrogen of the carboxyl group is absent.

In the literature there are only tentative statements concerning the possibility of copolymerization between methyl methacrylate and methyl vinyl ether [5]. From these results no information can be obtained concerning the ratio in which the original monomers will enter into copolymerization. In the present paper we give the results of a study of the copolymerization of methyl methacrylate with ethyl and butyl vinyl ethers, a wide range of monomer ratios being used. In this case, as in that of methacrylic acid, the copolymerization was smoothly effected in presence of benzoyl peroxide. Our explanation of this process is that methyl methacrylate contains the conjugated system $-\text{C}=\text{C}-\text{C}=\text{O}$, which is readily activated by oxygen [6] or by the free radicals formed by the decomposition of benzoyl peroxide [7], and that it initiates the chain according to Scheme 1 or 2, i.e., the function of benzoyl peroxide is more limited than it is considered to be by Gelisen and Hermans [8].



As our investigations have shown, compounds containing a conjugated system are suitable for copolymerization with alkyl vinyl ethers in presence of benzoyl peroxide. Hence, in the selection of components for copolymerization with alkyl vinyl ethers, we may take as one criterion the presence of conjugated double bonds in the original compound. The establishment, however, of a free-radical mechanism for the polymerization and copolymerization of vinyl ethers deserves close attention in its relation to the fact that the vinylation reactions of Favorsky and Shostakovsky [9] have opened up wide possibilities for the preparation of compounds containing both multiple bonds and various functional groups.

The present investigation has shown that increase in the concentration of the alkyl vinyl ether in the reaction mixture increases its content in the copolymer obtained. The structure of the latter may be represented as follows:



The presence in the molecule of alkyl vinyl ether units affects the solubility, fusibility, and outward appearance of the copolymers. The results of the elementary analysis of these copolymers show that, according to the ratio of the original components, they may contain 6-21 mole-% of alkyl vinyl ether units.

The supposition that the original components may undergo separate polymerization was not confirmed, i.e., the reaction product was a copolymer, and did not contain methyl methacrylate polymers or alkyl vinyl ether polymers. There is a somewhat incorrect statement in the literature concerning the part played by vinyl ethers in copolymerization processes [10], it being described as merely the termination of chains formed by compounds that readily polymerize by the free-radical mechanism, which, in the opinion of these authors, leads to the formation of compounds of low molecular weight. This view is apparently associated with the fact that, before our investigations [11], alkyl vinyl ethers were regarded as compounds that could not polymerize by a free-radical mechanism [12-15].

Our investigations have shown that copolymers of methyl methacrylate with alkyl vinyl ethers have molecules that are similar in size to those of the corresponding polymers of the methyl methacrylate component. The relative degrees of polymerization and copolymerization of our products were estimated by comparison of the viscosities of solutions of these polymers and copolymers, and it was found that in some cases the viscosities of solutions of the copolymers were equal to, and in other cases higher than, the viscosities of solutions of methyl methacrylate polymers prepared under the same conditions (see Tables 2 and 4).

As shown in the experimental part of this paper (Tables 1 and 3), the yield of polymer falls as the concentration of methyl methacrylate falls and as that of the vinyl ether rises; at the same time qualitative changes occur owing to rise in the number of alkyl vinyl ether units (Tables 2 and 4). We may, therefore, suppose that methyl methacrylate carries the function of chain initiation. Elementary analysis indicates a greater content of methyl methacrylate units in the molecule, and this is confirmed by estimation of the monomers that have not entered the reactions. The balance sheet of the products of the polymerization reaction shows that methyl methacrylate, alkyl vinyl ether, and copolymer are present. The differences found in the physical properties of the polymer of methyl methacrylate and those of the copolymers confirm that copolymerization does indeed occur. These differences are concerned with solubility and fusibility, and they grow as the number of alkyl vinyl ether units present in the molecular chain increases.

Hence, it has been shown, on the basis of yields, elementary composition, solubility, and other physico-chemical properties of the copolymers, that methyl methacrylate copolymerizes with alkyl vinyl ethers in presence of benzoyl peroxide.

EXPERIMENTAL

The starting materials were methyl methacrylate, b.p. 99.5-100°; n_D^{20} 1.4150; d_4^{20} 0.936; and ethyl vinyl ether, b.p. 35.9°; n_D^{20} 1.3778; d_4^{20} 0.7533; and butyl vinyl ether, b.p. 93.5-93.7°; n_D^{20} 1.4027; d_4^{20} 0.7791. The monomers were always freshly distilled for use in the polymerization reactions. Benzoyl peroxide was purified by two reprecipitations by methanol from chloroform solution.

Experimental Procedure

The copolymerization was carried out in glass tubes, which were heated in a thermostat at $60 \pm 1^\circ$. The reaction mixture consisted of 25 g altogether of the monomers, taken in various molar ratios, and 0.2% on the total weight of monomers of benzoyl peroxide. The process proceeded continuously until solid or highly viscous products were

obtained. At the end of the process the tubes were cooled to 0°. Control experiments were carried out under the same conditions on the polymerization in presence of benzoyl peroxide of the pure monomers: methyl methacrylate, and ethyl and butyl vinyl ethers. The purification and treatment of the reaction products were carried out as follows: they were dissolved in acetone and precipitated by methanol, dissolution and precipitation being repeated until there was a negative reaction for acetaldehyde with Schiff's reagent; the polymers and copolymers were then dried to constant weight.

The selective solubilities of the polymers and copolymers obtained were then determined. After treatment with selective solvents, the polymers and copolymers were precipitated with methanol, dried to constant weight, and analyzed for C and H. On the basis of the results, the compositions of the copolymers were calculated. Also, their fusibilities and viscosities were determined [16].

In all tests on the copolymers, a control sample of polymethyl methacrylate was taken for comparison. In order to check the ability of the monomers used to undergo free-radical polymerization, the following control tests were made.

1. A study of the tendency of methyl methacrylate to undergo polymerization in presence of benzoyl peroxide was carried out by the above-described procedure, the duration of the reaction being 40 hours. This polymer was soluble in acetone, and appreciably less soluble in benzene and dioxane. The polymer partly dissolved in boiling ethanol, and it dissolved completely in a boiling mixture of butyl alcohol and butyl vinyl ether; when the solutions were cooled it was reprecipitated. It was insoluble in alkyl vinyl ethers. The purified polymer was found to contain the following amounts of carbon and hydrogen:

Found %: C 60.24; 60.28; H 8.30; 8.28
Calculated %: C 59.99; H 8.00

2. Ethyl and butyl vinyl ethers were each heated in presence of benzoyl peroxide for 40 hours. After fractionation, the original ethers were recovered, and a very small residue of resinified material remained; it was insufficient for quantitative investigations. We give below some of the results of investigations on the copolymerization of alkyl vinyl ethers with methyl methacrylate.

Copolymerization of Methyl Methacrylate with Ethyl Vinyl Ether

The amounts taken for the copolymerization were 7.9 g of methyl methacrylate and 17.1 g of ethyl vinyl ether (i.e., a molar ratio of 1:3). The duration of heating was 40 hours. The contents of the tube became highly viscous. The conditions for the copolymerization and the purification are described above. It was found that the copolymer was soluble in a hot 85:15 mixture of ethanol and dioxane, and the solution remained clear when cold. At a similar concentration polymethyl methacrylate did not dissolve completely in the hot solvent, and when the solution was cooled it was reprecipitated. The copolymer was dissolved in the mixture of ethanol and dioxane, precipitated from solution with methanol, dried to constant weight, and subjected to microanalysis.

The above-described procedure for the copolymerization of methyl methacrylate with ethyl vinyl ether was carried out also at other monomer ratios. The monomer ratios and yields are given in Table 1, in which the solubilities of the copolymers in the mixture of ethanol and dioxane are also given. The microanalytical results on the copolymers are given in Table 2.

TABLE 1
Monomer Ratios and Yields of Copolymers

No.	Molar ratios		Yield of polymer or co-polymer (%)	Solubility in 15:85% dioxane/ethanol
	$\text{CH}_2=\text{C}(\text{COOCH}_3)\text{CH}_3$	$\text{CH}_2=\text{CHOC}_2\text{H}_5$		
1	1.0	—	97.32	Insoluble
2	0.75	0.25	86.30	"
3	0.50	0.50	60.1	Soluble
4	0.25	0.75	33.5*	"
5	—	1.00	**	

* Apart from copolymer, 60% of ethyl vinyl ether and 51% of methyl methacrylate were isolated.

** 96.3% of ethyl vinyl ether was isolated.

When the copolymers were heated in crucibles, some of them melted, forming vitreous masses. This behavior was particularly characteristic for copolymers containing a high proportion of alkyl vinyl ether units.

Copolymerization of Methyl Methacrylate with Butyl Vinyl Ether

The amounts taken for the copolymerization were 6.25 g of methyl methacrylate and 18.75 g of butyl vinyl ether (i.e., a molar ratio of 1:3). The duration of heating was 40 hours. The contents of the tube became highly viscous. The copolymerization conditions and the method of purification of the copolymer are described above. The copolymer did not dissolve completely when heated with a mixture of ethanol and dioxane, but was readily soluble in a 1:1 mixture of butyl alcohol and butyl vinyl ether; polymethyl methacrylate was

TABLE 2

Compositions of Copolymers

No.	Molar ratios		Amount of		Mol. proportions of units in copolymer (%)		Viscosity	
	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_2=\text{C} \\ \\ \text{COOCH}_3 \end{array}$	$\begin{array}{c} \text{CH}_2=\text{CH} \\ \\ \text{OC}_2\text{H}_5 \end{array}$	C (%)	H (%)	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_2-\text{C} \\ \\ \text{COOCH}_3 \end{array}$	$-\text{CH}_2-\text{CH}-$ OC_2H_5	$\eta_{\text{Stokes/sec}}$	η_{rel}
1	1.0	—	60.24	8.30	—	—	0.011	1.5011
			60.28	8.28	—	—	—	—
2	0.75	0.25	60.22	8.35	93.45	6.55	0.041	5.4992
			60.43	8.44	—	—	—	—
3	0.5	0.5	60.61	8.17	85.35	14.65	0.0268	3.5819
			60.85	8.36	—	—	—	—
4	0.25	0.75	61.13	8.33	78.35	21.65	0.013	1.8001
			61.05	8.46	—	—	—	—
5	—	1.0	—	—	—	—	—	—

Monomer ratios of 1.0 and 0.75 were found to give copolymers soluble in methanol, but found to be insoluble in the latter solvent. In this, as in the previous, series of experiments, no polymer of methyl methacrylate was isolated. The copolymer was precipitated from solution with methanol and dried to constant weight. The carbon and hydrogen contents were then determined by microanalytical methods.

The copolymerization of methyl methacrylate with butyl vinyl ether was carried out also at other monomer ratios. The yields of copolymers are given in Table 3.

TABLE 3
Monomer Ratios and Yields of Copolymers

No.	Molar ratios		Yield of polymer or copolymer (%)	Solubility in 50:50 butyl alcohol/butyl vinyl ether
	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_2=\text{C} \\ \\ \text{COOCH}_3 \end{array}$	$\begin{array}{c} \text{CH}_2=\text{CH} \\ \\ \text{OC}_2\text{H}_5 \end{array}$		
1	1.0	—	97.32	Insoluble
2	0.75	0.25	76.5	Soluble
3	0.50	0.50	60.7	"
4	0.25	0.75	27.0	"
5	—	1.0	*	—

* Unchanged butyl vinyl ether was recovered.

TABLE 4
Compositions of Copolymers

No.	Molar ratios		Amount of		Mol. proportions of units in copolymer (%)		Viscosity	
	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_2=\text{O} \\ \\ \text{COOCH}_3 \end{array}$	$\begin{array}{c} \text{CH}_2=\text{CH} \\ \\ \text{OC}_2\text{H}_5 \end{array}$	C (%)	H (%)	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_2-\text{C} \\ \\ \text{COOCH}_3 \end{array}$	$-\text{CH}_2-\text{CH}-$ OC_2H_5	$\eta_{\text{Stokes/sec}}$	η_{rel}
1	1.00	—	60.24	8.30	100	—	0.011	1.5016
			60.28	8.28	—	—	—	—
2	0.75	0.25	61.93	8.47	86.4	13.6	0.015	2.0299
			61.73	8.32	—	—	—	—
3	0.50	0.50	61.65	8.67	86.4	13.6	0.016	2.1719
			61.61	8.47	—	—	—	—
4	0.25	0.75	62.68	8.92	76.33	23.67	0.0126	1.6932
			62.99	9.02	—	—	—	—
5	—	1.00	—	—	—	—	—	—

SUMMARY

1. A study has been made of the copolymerization of methyl methacrylate with alkyl vinyl ethers in presence of benzoyl peroxide at various monomer ratios.

2. Copolymers of methyl methacrylate with alkyl vinyl ethers have been prepared.

3. It has been shown that, in presence of benzoyl peroxide, copolymerization may be effected between alkyl vinyl ethers and compounds containing the system of double bonds: $-C=C-C=O$.

4. In the copolymerization of methyl methacrylate with alkyl vinyl ethers in presence of benzoyl peroxide, no polymers of methyl methacrylate were detected.

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* See Consultants Bureau Translation, page 931.

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CHEMICAL METHOD OF INVESTIGATING THE METAL-HYDROGEN

NATURE OF A SKELETAL NICKEL CATALYST

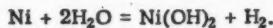
L. Kh. Freidlin and K. G. Rudneva

By analogy to the promoting effect of gases on metal films [1], it may be supposed that hydrogen plays a determining role in the activity of a skeletal (Raney) catalyst. It is known that such catalysts contain considerable amounts of hydrogen, attaining several hundredths of a milliliter per gram of nickel. It was necessary to work out a method that would make it possible to establish a relationship between the activity of a skeletal catalyst and the presence of hydrogen in the catalyst. The physical method of removing hydrogen by prolonged continuous pumping at high temperature has the serious defect that under these conditions the structure of the catalyst may be changed, so that it may be almost impossible to separate the effect of hydrogen removal on the properties of the catalyst from the effect of the thermal treatment. Unlike the physical method, the chemical method enables the hydrogen removal to be carried out at close to room temperature, at which the physical structure of the catalyst does not alter, and it is permissible, therefore, to study the changes in the properties of a skeletal catalyst from which hydrogen has been removed chemically by means of substances that can be hydrogenated.

The correct selection of substances suitable for this purpose is extremely important. The hydrogen-removing agent must rapidly and completely extract the hydrogen present in the nickel. The reagent and its hydrogenation products must not react with the metal or block its active surface, and they must be readily analyzed. After the process, the catalyst must be quantitatively separated from the hydrogenatable substance by filtration, and must be analyzed. If the hydrogenatable substance is volatile, then it is difficult to avoid losses, and the agent must, therefore, have a high boiling point. The previously used hydrogen-removing agents — butyl vinyl ether, nitrobenzene, and cyclopentene [2] — were readily volatile, not readily accessible, or difficult to analyze. We have succeeded in finding a hydrogen-removing agent that does not suffer from these defects, and in establishing the optimum conditions for the removal of hydrogen from the catalyst.

The chemical method for the removal of hydrogen serves at the same time as a method for the determination of the amount of chemically active hydrogen in the catalyst. The results of duplicate tests on the hydrogen content of the catalyst generally agree within 1-2%. By means of the chemical method of hydrogen removal we have established the nonequivalence of the two forms of hydrogen contained in the catalyst and the existence of a relationship between the activity of a catalyst and its hydrogen content [2]. Sokolsky and co-workers [3] have reached the same conclusion by the use of an independent potentiometric method. On the basis of results obtained by the chemical method we predicted the possibility of restoring the activity of an inert catalyst by treatment with hydrogen, and we have confirmed this experimentally [4].

We have recently shown that the activity of a skeletal nickel catalyst that has been partly "dehydrogenated" and deactivated by treatment at 300° in a vacuum in absence of organic hydrogen-removing agents can also be restored by treatment with hydrogen. The results obtained by the physical method are, therefore, similar to those obtained by the method of chemical removal of hydrogen. Aubry [5] has suggested that the reducing action of skeletal nickel in aqueous medium on sulfites, thiosulfates, selenites, and other compounds at room temperatures is to be explained by its ability to react with evolution of hydrogen:



The film of nickel hydroxide protects the metal and preserves its activity.

We have established by special experiments that, after treatment with water vapor for two hours at temperatures of up to 200°, the catalyst fully retains its activity. Hence, even at this high temperature a skeletal nickel catalyst does not react with water vapor and does not become covered with a film of hydroxide that will block its active surface. We have shown also that the amount of determinable hydrogen in the nickel does not depend on whether the benzoquinone with which it has been treated was dissolved in moist dioxane or in dioxane that had been twice distilled over sodium.

Conditions for the Removal of Hydrogen from the Catalyst by means of Benzoquinone

It was found that benzoquinone most satisfactorily fulfills the requirements for a hydrogen-removing agent for use in the chemical method. It is convenient to treat the catalyst with benzoquinone in dioxane, in which the intermediate and final reaction products, quinhydrone and hydroquinone, are also readily soluble. The dioxane was freshly distilled, and did not contain peroxy compounds. The reaction was carried out in a hydrogenation flask attached to a powerful shaker and connected to a gas buret. The flask was provided with a jacket for heating, and with two tubes for the introduction of catalyst and hydrogenatable substance and for the entry and exit of gases. A No. 3 glass filter was fused into one of the outlet tubes. The flask was heated with water taken from an ultrathermostat and circulated through the jacket. A spoonful of the catalyst paste, leveled by means of a glass rod, was taken for each experiment, so that practically equal weights of catalyst were taken on each occasion.

Removal of hydrogen from the catalyst was carried out as follows: Air was displaced from the flask with hydrogen, and in a current of hydrogen, the catalyst was washed through a funnel into the flask with the aid of 5-10 ml of solvent. The outlet tube was closed with a ground stopper, the shaker was switched on, and the catalyst was saturated with hydrogen. When the absorption of hydrogen ceased or did not exceed 0.1 ml per minute, saturation of the catalyst was regarded as complete. Hydrogen was carefully displaced from the flask with nitrogen, and, in a current of nitrogen, a definite volume of a 3% solution of benzoquinone in dioxane was introduced. The motor was switched on, and shaking began. Under these conditions benzoquinone could be hydrogenated to hydroquinone, but only by hydrogen contained in the catalyst. Hydrogenation to cyclohexanediol would require a much higher temperature.

After treatment of the catalyst with benzoquinone in an atmosphere of nitrogen, the catalyst was filtered off and washed 5-6 times with dioxane to effect complete removal of benzoquinone and its hydrogenation products. The completeness of the removal of benzoquinone was checked by the reaction with iodine in an alkaline medium [6]. The washings were united with the main filtrate, and the contents of hydroquinone and of residual benzoquinone were determined iodometrically [7, 8]. From the results of this analysis, the amount of hydrogen extracted from the catalyst by benzoquinone was calculated. The activity of the catalyst was then determined.

The removal of hydrogen from the catalyst by means of benzoquinone in absence of an external hydrogen source led to breakdown of its active structure and to deactivation. At 20°, fairly complete deactivation of the catalyst was attained only after treatment for 120 minutes with benzoquinone (an excess with respect to the hydrogen in the catalyst). When the temperature was raised to 60°, the time required for the deactivation of the catalyst was reduced to 60 minutes. The catalyst, removed from the liquid and washed carefully, would not absorb hydrogen and was completely inactive for the hydrogenation of organic compounds at 20°.

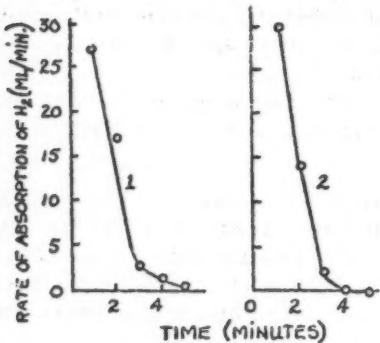


Fig. 1. Rate of hydrogenation of 0.2495 g of phenyl vinyl ether in two successive experiments (1 and 2) in alcohol at 20° with 1 g of skeletal nickel catalyst.

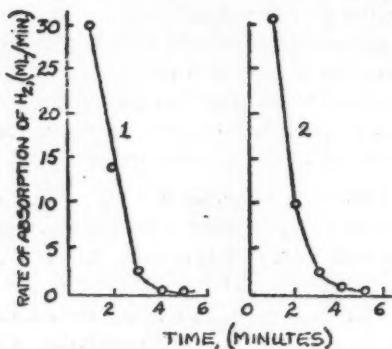


Fig. 2. Rate of hydrogenation of 0.2495 g of phenyl vinyl ether in alcohol at 20° with 1 g of skeletal nickel catalyst: 1) freshly prepared; 2) after keeping for 6 months under water.

Method of Testing the Activity of the Catalyst

The activity of the catalyst was determined from the rate of hydrogenation of phenyl vinyl ether in ethanol at 20° under normal pressure. The phenyl vinyl ether had b.p. 155-156° and n_{D}^{20} 1.5225. This substance does not remove hydrogen from the catalyst in the process of hydrogenation, it is of low volatility, and it is readily analyzed iodometrically. It was established by special experiments that the activity of a given portion of catalyst does not fall in a series of successive hydrogenations of phenyl vinyl ether (Fig. 1).

The samples of catalyst were prepared by a two-hour leaching of a 50% Ni-Al alloy with 20% caustic soda at 100-105°. In one of these, in the freshly prepared form, 176 ml of hydrogen was found per gram of catalyst. After being kept for six months under water, it was found to contain 173 ml of hydrogen per gram, and its activity had not changed (Fig. 2).

Fig. 3 shows the rate curves for the hydrogenation of phenyl vinyl ether at 20° in presence of various amounts of catalyst: 0.25, 1, and 2 g. It will be seen from Fig. 3 that, when the amount of catalyst is increased from 1 g to 2 g, the rate of the reaction remains practically unchanged. On the other hand, when the amount of catalyst is reduced to 0.25 g, not only the reaction rate, but also the character of the kinetics changes. The apparent zero-order reaction that is found when there is insufficient catalyst in the system may be explained by the hypothesis that the reaction rate is limited in this case by the rate at which hydrogen is activated on the catalyst. In our experiments, 1 g of catalyst was used.

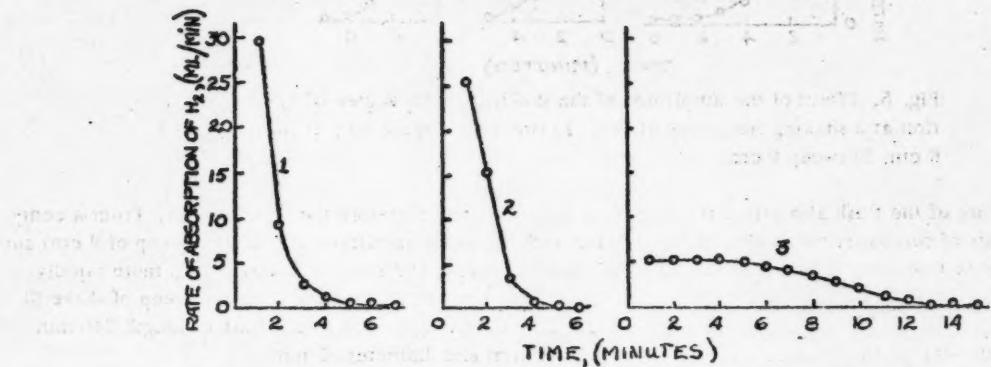


Fig. 3. Rate of hydrogenation of 0.2495 g of phenyl vinyl ether at 20° in alcohol:
1) with 2 g of skeletal nickel catalyst; 2) with 1 g; 3) with 0.25 g.

Effect of the Amplitude of Shaking and the Dimensions of the Flask on the Degree of Agitation and the Rate of Hydrogenation

In order to exclude the effect of the rate of diffusion of the reacting components to the catalyst surface when studying the kinetics of the reaction, we carried out a series of experiments with the object of determining the effect of the amplitude of shaking and the dimensions of the flask on the degree of agitation. A study was made of the rate of hydrogenation of 0.2495 g of phenyl vinyl ether in 15 ml of alcohol in presence of 1 g of catalyst. At first experiments were carried out in a flask of smaller dimensions: length 150 mm and internal diameter 30 mm. It will be seen from the curves in Fig. 4 that with a shaking frequency of 470 complete oscillations the reaction rate is considerably higher when the sweep of the shake is 9 cm than when it is 3 cm. An analogous increase in reaction rate is observed when the frequency of shaking is increased. Comparing the results of three experiments carried out at 880

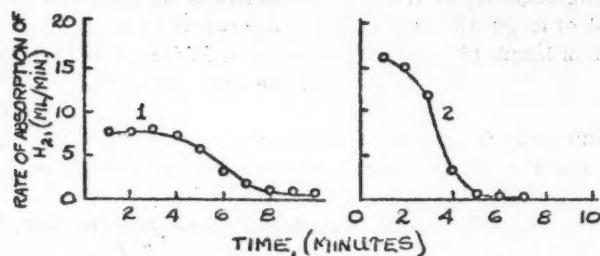


Fig. 4. Effect of the amplitude of the shaking on the degree of agitation at a shaking frequency of 470: 1) total sweep of shake 3 cm; 2) total sweep 9 cm.

oscillations per minute (Fig. 5), we see that in the experiment with the shortest sweep (3 cm) the reaction is slower than in the experiment with a longer sweep (6 cm). Further increase in the sweep of the shake (9 cm) did not increase the reaction rate.

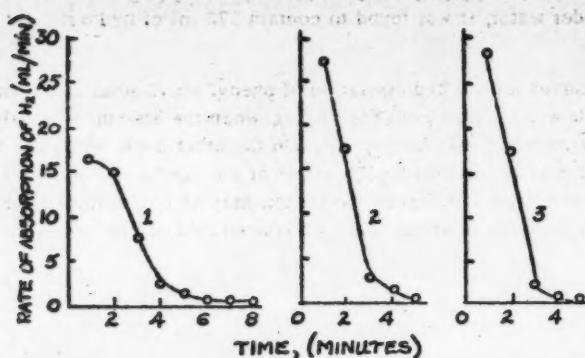


Fig. 5. Effect of the amplitude of the shaking on the degree of agitation at a shaking frequency of 880: 1) sweep of shake 3 cm; 2) sweep 6 cm; 3) sweep 9 cm.

The dimensions of the flask also affect the degree of agitation, and therefore the reaction rate. From a comparison of the results of two experiments (Fig. 6) carried out with the same amplitude of shaking (sweep of 9 cm) and with the same shaking frequency (470), it follows that in a flask of length 180 mm the reaction goes more rapidly than in a flask of length 150 mm. A similar effect was obtained in an experiment with a shorter sweep of shake (3 cm), but with a higher shaking frequency (880) (Fig. 7). The rate of hydrogenation in the flask of length 240 mm and diameter 40 mm was greater than in the flask of length 150 mm and diameter 30 mm.

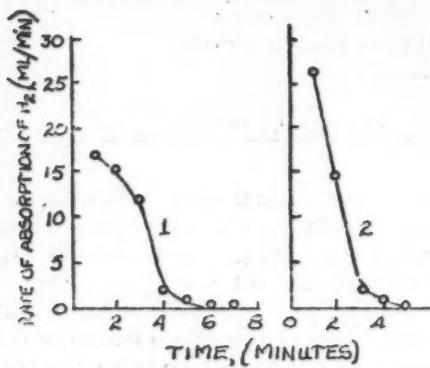


Fig. 6. Effect of the dimensions of the flask on the degree of agitation at a shaking frequency of 470 and a sweep of 9 cm: 1) flask of length 150 mm and diameter 30 mm; 2) flask of length 180 mm and diameter 30 mm.

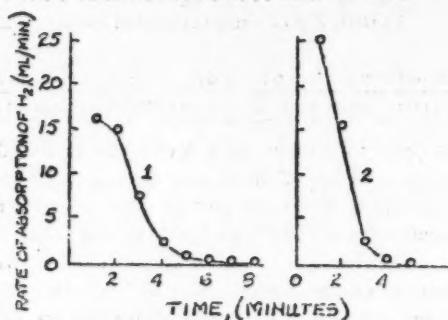


Fig. 7. Effect of the dimensions of the flask on the degree of agitation at a shaking frequency of 880 and a sweep of 3 cm: 1) flask of length 150 mm and diameter 30 mm; 2) flask of length 240 mm and diameter 40 mm.

When the shakes are sufficiently frequent (880) and long (6 cm), the reaction proceeds at the same rate in the large (length 240 mm, diameter 40 mm) and the small (length 150 mm, diameter 30 mm) flasks, as will be seen from Fig. 8. Fig. 9 shows that with a still longer sweep of shake (10.5 cm), even at a lower frequency (700), the rate of the reaction is practically independent of the dimensions of the flask, being identical in the small and in the large flasks.

Thus, sufficiently vigorous agitation in the system can be ensured not only by increase in the rate of shaking, but also by changes in the amplitude of the shake and in the dimensions of the reaction vessel.

SUMMARY

1. A chemical method for the removal of hydrogen from a skeletal nickel catalyst is described; it serves at the same time as a method for the determination of the amount of chemically active hydrogen contained in the metal.

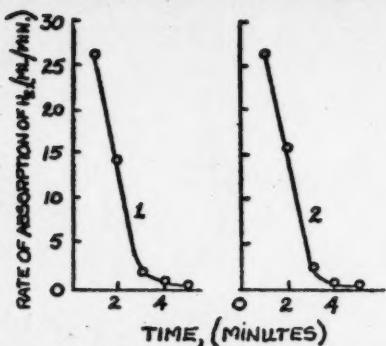


Fig. 8. Rate of hydrogenation of 0.2495 g of phenyl vinyl ether in alcohol at 20° in presence of 1 g of skeletal nickel catalyst at a shaking frequency of 880 and a sweep of shake of 6 cm: 1) flask of length 150 mm and diameter 30 mm; 2) flask of length 240 mm and diameter 40 mm.

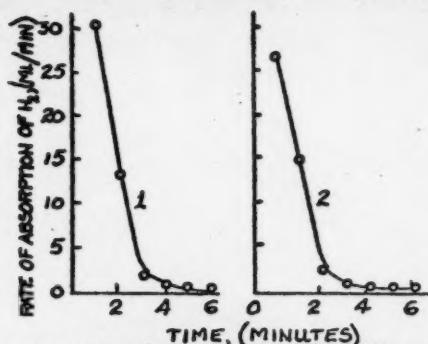


Fig. 9. Rate of hydrogenation of 0.2495 g of phenyl vinyl ether in alcohol at 20° in presence of 1 g of skeletal nickel catalyst at a shaking frequency of 700 and a sweep of shake of 10.5 cm: 1) flask of length 150 mm and diameter 30 mm; 2) flask of length 180 mm and diameter 30 mm.

2. The method makes it possible to establish a relationship between the activity of a skeletal catalyst and its hydrogen content.

3. The effect of the amount of catalyst, the amplitude of the shake, and the dimensions of the flask on the reaction rate is also investigated.

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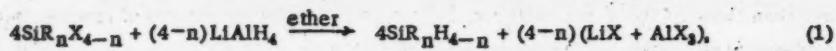
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part, and decomposition products of such silanes. Brought to commercial silicon plants, monochloride and dichloride of silicon will be used to satisfy the needs of the industry.

SYNTHESIS OF SOME ALKENYL- AND ALKYL-SILANES AND THEIR DERIVATIVES

V. A. Ponomarenko and V. F. Mironov

In 1947 Schlesinger and coworkers [1] proposed a convenient method for the preparation of silanes of the type $RSiH_3$ and R_2SiH_2 by reduction of the corresponding halosilanes with lithium aluminum hydride:



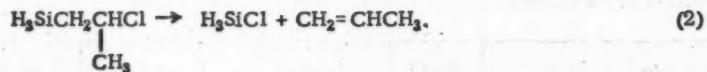
(R is alkyl or aryl, and $n = 1, 2, \text{ or } 3$).

The discoverers of the method, and also other investigators [2], have noted that in certain cases lithium hydride can be used for this purpose, but the resulting yield of alkylsilanes was then lower, and it was found that an elevated temperature and a three- or four-fold excess of lithium hydride were necessary.

In this series of silanes, compounds containing unsaturated radicals, or radicals containing halogen, are unknown. It might be thought that both $LiAlH_4$ and LiH could be used for their synthesis. When, however, $LiAlH_4$ is used, it is quite possible that the products will undergo polymerization or isomerization under the influence of the considerable amounts of AlX_3 formed in the reaction of Equation 1. Allyltrimethylsilane, for example, polymerizes vigorously in presence of $AlCl_3$ under mild conditions [3], and (chloromethyl)trimethylsilane readily undergoes rearrangement to chloroethyltrimethylsilane [4]. Hence, in order to avoid these undesirable reactions, all reductions were effected with lithium hydride, which, moreover, is considerably more readily accessible than $LiAlH_4$. The expediency of making extensive application of lithium hydride has recently been pointed out by one of us and Petrov [5] with respect to the synthesis of the silicon analogs of propane, butane, pentane, and cyclohexane.

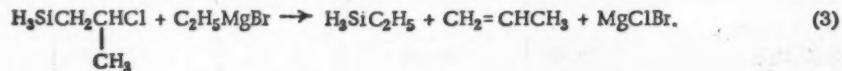
Continuing this line of investigation, we have found that $(C_2H_5)_2Si(OC_2H_5)_2$ is reduced by lithium hydride to $(C_2H_5)_2SiH_2$. This first indication of the possibility of the replacement of an ethoxy group attached to silicon by hydrogen is important also because $LiAlH_4$, which cannot form the harmful AlX_3 with alkoxy silanes, may be used if desired. The reduction of allyltrichlorosilane with lithium hydride resulted in a relatively low yield (37%) of allylsilane. Diallylsilane was obtained similarly in 37% yield. The compounds obtained are quite stable liquids having an odor that is characteristic for the whole series of allylsilanes [6]. Diallylsilane combines quantitatively at the double bonds with thiocyanogen, without any side reactions.* This fact is of importance in that the quantitative determination of the unsaturation of allylsilanes by the bromine-number method gives indefinite results, since bromine causes β -decomposition and reacts with the Si-H bond.

Allylsilane slowly combines with hydrogen chloride. An attempt to distill the chloro compound so formed resulted in its decomposition at about 80° .**



CH₃

In a vacuum (2-chloropropyl)silane can be distilled without decomposition. When it is treated with Grignard reagents — allylmagnesium bromide and ethylmagnesium bromide — reaction occurs. However, although no signs of β -decomposition are noted in the case of allylmagnesium bromide (absence of gas evolution), with ethylmagnesium bromide β -decomposition occurs, as is shown by the vigorous evolution of gas:



CH₃

In neither case was it found possible to isolate any individual condensation products, formed in accordance with the scheme for the reaction of β -halo compounds with $RMgX$ that we have investigated previously [6, 8, 9], although a considerable amount of high-boiling ($100-160^{\circ}$) products was formed. The thermal instability and β -decomposition

* The addition of thiocyanogen was kindly carried out by A. A. Bugorkovskaya, who has developed the method and has determined thiocyanogen numbers for more than 25 alkenylsilanes.

** It is very probable that this reaction will provide a convenient method for the preparation of difficultly accessible [7] halosilanes of the type H_3SiX .

of this chloro compound under the influence of Grignard reagents proves that it is a β -chloro compound, i.e., that HCl adds to allylsilane (as also to other allylsilanes [3, 6, 8, 9, 10]) according to Markovnikov's rule.

As we now had a β -chloro compound of the structure indicated, it was of interest to prepare an α -chloro compound for comparison of properties. With this object, $\text{Cl}_3\text{SiCH}_2\text{Cl}$ was reduced with lithium hydride. The course of the reaction was such that only chlorine attached to silicon was replaced by hydrogen, the chlorine attached to carbon being left untouched. The resulting α -chloro compound, unlike the β compound, was a stable liquid that did not decompose when distilled or stored. Both chloro compounds were of pleasant odor, thus indicating absence of chlorine attached to silicon. Among the physical properties of the sila-hydrocarbons obtained, the melting points and molecular refractions are of interest.

It is clear from the work of Petrov and Chemyshev [11] that the melting points of tetra-substituted silanes are lower than those of the structurally similar tetraalkylmethanes. It was of interest to determine the melting points of straight-chain silanes and to determine the effect of the presence of double bonds and of the position of the silicon atom in the chain. For this purpose, and also in order to make a comparison of other physical properties, hexylsilane and dipropylsilane were synthesized by the above-described method [5]. The melting points of diallylsilane, di-propylsilane, and hexylsilane are given, together with that of heptane for comparison, in Table 1.*

TABLE 1

Substance	Formula	M.p. (°C)
Diallylsilane	$\text{CH}_2=\text{CHCH}_2\text{SiH}_2\text{CH}_2\text{CH}=\text{CH}_2$	-115
Dipropylsilane	$\text{CH}_3\text{CH}_2\text{CH}_2\text{SiH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	-113
Hexylsilane	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{SiH}_3$	-98
Heptane	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	-90.6

It will be seen from Table 1 that the introduction of double bonds into the hydrocarbon chains of silanes (for example, passing from dipropyl- to diallylsilane) has practically no effect on the melting point. On the other hand, the movement of the silicon atom from the periphery (hexylsilane) to the center (dipropylsilane) results in a considerable lowering of the melting point. Also, these silicon analogs of heptane melt lower than heptane itself.

Comparison of the calculated [12] and found values of the molecular refraction for mono- and di-allylsilanes reveals a quite definite discrepancy, such as was observed previously for a number of substituted allylsilanes [6, 8, 9]. This discrepancy is to be explained by the fact that the value assumed in the literature [12] for the refraction of the Si-C bond is 2.50 ml/mole for all alkyls, although this value is satisfactory only for methyl. On the basis of experimental data for a large number of allyl-substituted silanes, we have found the refraction of the Si-C bond (when C belongs to allyl) to be 2.68 ml/mole.

Analysis of the data for a series of alkyltriethylsilanes [13] shows that, for the ethyl radical also, the value for the Si-C bond differs somewhat from the value given above and should evidently be taken to be 2.38 ml/mole. If we take these corrections into consideration, then, as Table 2 shows, for the majority of sila-hydrocarbons containing ethyl and allyl radicals, the discrepancy between calculated and found refractions almost disappears.

TABLE 2

Formula of compound	MR					Literature reference
	found	calculated [12]	Δ	calcd. by us	Δ	
$(\text{C}_2\text{H}_5)_4\text{Si}$	48.34	48.8	-0.46	48.32	+0.02	[13]
$(\text{C}_2\text{H}_5)_2\text{SiH}_2$	30.63	30.80	-0.17	30.56	+0.07	This investigation
$(\text{C}_2\text{H}_5)_3\text{SiC}_3\text{H}_5$	52.72	52.96	-0.24	52.78	-0.06	[8]
$\text{C}_6\text{H}_5(\text{CH}_3)_2\text{SiC}_3\text{H}_5$	59.07	58.89	+0.18	59.07	0.00	[6]
$(\text{CH}_3)_3\text{SiC}_3\text{H}_5$	39.20	39.07	+0.13	39.25	-0.05	[3]
$\text{H}_3\text{SiC}_3\text{H}_5$	26.15	25.96	+0.19	26.14	+0.01	This investigation
$(\text{CH}_3)_2\text{Si}(\text{C}_3\text{H}_5)_2$	48.20	47.86	+0.34	48.22	-0.02	[9]
$\text{H}_2\text{Si}(\text{C}_3\text{H}_5)_2$	39.48	39.12	+0.36	39.48	0.00	This investigation
$\text{CH}_3\text{Si}(\text{C}_3\text{H}_5)_3$	57.20	56.65	+0.55	57.19	+0.01	[9]
$\text{C}_6\text{H}_5\text{Si}(\text{C}_3\text{H}_5)_3$	76.90	76.47	+0.43	77.01	-0.11	[6]
$\text{Si}(\text{C}_3\text{H}_5)_4$	66.16	65.44	+0.72	66.16	0.00	[14]

* The melting point determinations were carried out by V. A. Volnova by the method of solidification and melting curves. We take the opportunity of expressing our sincere thanks to her.

EXPERIMENTAL

Lithium Hydride

Lithium hydride was prepared from lithium and hydrogen at 690-700° in an apparatus having an output of about 150 g lithium hydride per day. In principle, this apparatus was similar to that already described by Albert and Mahé [15], but differed from it in being simpler to construct and use. The differences were essentially as follows: a) gas heating was replaced by electric, and the reaction temperature was maintained constant within $\pm 10^\circ$ by means of an electronically operated regulator; b) the reactor was appreciably simplified, water-cooling of the flanges being dispensed with, the protective jacket removed, rubber packing replaced by copper, and the bolts of the reactor head made hollow to enable them to be water-cooled; c) one beaker, instead of two, was used in the reactor; d) so that the reactor could be cooled more rapidly at the end of the experiment, the electric furnace was made of two insulated halves joined together by hinges so that it could be opened out for removal.

The yield of LiH was quantitative; about 1 kg was prepared. It was carefully ground in a steel ball mill filled with steel balls. At first it was passed through a sieve having 200 mesh per inch, but it was later found that it could be used successfully in the reaction without being sieved, since the milling in the ball mill rendered it sufficiently fine.

Dibutyl and Diisopentyl Ethers

The ethers were prepared in the usual way from the alcohols, dried over CaCl_2 and over sodium, and distilled over a small amount of LiH through a 20-plate column.

Allyltrichlorosilane $\text{CH}_2=\text{CHCH}_2\text{SiCl}_3$

Allyltrichlorosilane was synthesized in two ways.

1. Direct synthesis [16]. Allyl chloride, diluted with nitrogen, was passed over silicon-copper alloy at 290-300°. The reaction tube rapidly became clogged with polymerization products. From 800 g of the crude mixture, 35 g of allyldichlorosilane, b.p. 96.0-98.0°, and 48 g of allyltrichlorosilane, b.p. 115.5-117.0°, were isolated. In addition HSiCl_3 , $\text{C}_3\text{H}_5\text{Cl}$, SiCl_4 , and higher-boiling products were always isolated.

2. Organomagnesium synthesis. A few milliliters of allyl bromide were added to 97 g (4 moles) of magnesium in 1500 ml of ether in a two-liter flask. When the reaction had started, the contents of the flask were stirred for 11 hours while addition was made (at about 100 drops per minute) of a mixture of 500 g (3 moles) of SiCl_4 and 242 g (2 moles) of allyl bromide. The contents of the flask were boiled for four hours, filtered, and fractionated, yielding 130 g (37.4%) of allyltrichlorosilane, b.p. 116-118° (737 mm); n_D^{20} 1.4455; In addition, 20 g of diallylchlorosilane, b.p. 165-170°, was obtained.

This method is considerably more convenient than the direct synthesis [16] and the synthesis requiring the preliminary preparation of allylmagnesium bromide [17].

Allylsilane $\text{CH}_2=\text{CHCH}_2\text{SiH}_3$

A mixture of 110 g of allyltrichlorosilane, 45 g of lithium hydride, and 150 ml of diisopentyl ether was prepared in a still incorporating a small fractionating column. Allylsilane was distilled over periodically and collected in a trap. After the reaction mixture had been boiled for two days, 16.5 g (37%) of allylsilane, b.p. 17.0-20.0° had collected. After fractionation through a 35-plate column the allylsilane had the following constants: b.p. 16.9° (736.3 mm); d_4^{20} 0.6764; n_D^{20} 1.4050; found MR 26.15; calculated MR 26.14.

Diallylsilane $(\text{CH}_2=\text{CHCH}_2)_2\text{SiH}_2$

Under similar conditions, 33 g of allyldichlorosilane and 10 g of lithium hydride in 50 ml of diisopentyl ether yielded 7.5 g of diallylsilane, which, after two fractionations through a 35-plate column, had the following constants: b.p. 103.7° (740.3 mm); d_4^{20} 0.7533; n_D^{20} 1.4420; found MR 39.48; calculated MR 39.48.

Found %: C 63.78; 63.86; H 10.67; Si 25.36; 25.17
 $\text{C}_6\text{H}_{12}\text{Si}$. Calculated %: C 64.21; H 10.78; Si 25.01

Yield of diallylsilane: 37%.

(2-Chloropropyl)silane $\text{H}_2\text{SiCH}_2\text{CHCl}_2$

Hydrogen chloride was passed through 15 g (0.2 mole) of allylsilane contained in a Drechsel bottle and cooled to -79° , until the weight increased by 10 g. The Drechsel bottle was then left in a freezing mixture in a Dewar

vessel overnight. The reaction product, after removal of HCl under vacuum, was found to be practically pure (2-chloropropyl)silane (n_D^{20} 1.4305), the yield being 18 g. When vacuum-distilled it gave no other fractions and had the following constants: b.p. 30.5° (140 mm); n_D^{20} 1.4305; d_4^{20} 0.8983; found MR 31.27; calculated MR 31.27.

Dipropylsilane ($C_3H_7)_2SiH_2$

A mixture of 35 g of dichlorodipropylsilane (b.p. 173-175°; prepared from $SiCl_4$ and C_3H_7MgBr), 15 g of lithium hydride, and 45 ml of dry diisopentyl ether was prepared in a still incorporating a small fractionating column. The reaction mixture was boiled, and the reaction product was distilled over periodically. A mixture (20 ml) of dipropylsilane and diisopentyl ether was collected, and this was fractionated over lithium hydride at 758 mm through a 20-plate column. Yield of dipropylsilane: 37% (from fractionation curve). The following fractions were obtained:

Fraction I, b.p. 32-110.4°; 2.4 ml; n_D^{20} 1.4009;

Fraction II, b.p. 110.4-111.0°; 5.9 ml; n_D^{20} 1.4110; d_4^{20} 0.7183

Fraction III, b.p. 110-149.0°; 1.8 ml; n_D^{20} 1.4105

Found: MR 40.18

Calculated: MR 40.06

These constants are in good agreement with data in the literature: b.p. 111°; d_4^{20} 0.7194; n_D^{20} 1.4112 [1].

Found %: C 62.03; 61.91; H 14.19; 14.03; Si 24.44; 24.14

Calculated %: C 61.99; H 13.87; Si 24.14

Hexylsilane $C_6H_{13}SiH_3$

The trichlorohexylsilane $C_6H_{13}SiCl_3$ required for the reduction was prepared in two ways: a) from $C_6H_{13}MgBr$ and $SiCl_4$, 378 g (64%) of b.p. 189-192° being obtained (the literature [3] gives b.p. 127° (98 mm)); and b) from 1-hexene (b.p. 62.5-64°) and trichlorosilane (b.p. 31-32°) in presence of benzoyl peroxide. In one of these experiments, 4.2 g of 1-hexene, 15 g of $HSiCl_3$, and 0.9 g of freshly recrystallized benzoyl peroxide were taken. The reaction was carried out at 100° in a glass test tube contained in a 50-ml autoclave; it was continued for several days. The product was 7 g of trichlorohexylsilane, b.p. 188-191°; yield 64% on 1-hexene taken.

For the preparation of hexylsilane, 35 g of trichlorohexylsilane, 17 g of LiH , and 50 ml of diisopentyl ether were taken. A mixture (20 ml) of hexylsilane and diisopentyl ether was collected. Fractionation through a 20-plate column at 751 mm yielded the following fractions:

Fraction I, b.p. 111.5-114.0°; 2.2 mg; n_D^{20} 1.4109

Fraction II, b.p. 114.0-114.5°; 10.0 mg; n_D^{20} 1.4129; d_4^{20} 0.7182

Fraction III, b.p. 114.5-148.0°; 4.2 mg; n_D^{20} 1.4122

Found: MR 40.35

Calculated: MR 40.32

Found %: C 62.00; 61.74; H 14.00; 13.70; Si 24.05; 24.32

Calculated %: C 61.99; H 13.87; Si 24.14

Yield of hexylsilane: 65% (from fractionation curve).

(Chloromethyl)silane H_3SiCH_2Cl

H_3SiCH_2Cl was prepared from 46 g of Cl_3SiCH_2Cl , 24 g of lithium hydride, and 95 ml of diisopentyl ether. The crude reaction product was collected in a trap.

Fractionation over LiH through a 35-plate column yielded 3.4 ml of H_3SiCH_2Cl , having the following constants: b.p. 30.5° (739 mm); d_4^{20} 0.9286; n_D^{20} 1.4157; found MR 21.76; calculated MR 22.01.

Found %: Cl 43.66; 43.36

Calculated %: Cl 44.01

Diethylsilane ($C_2H_5)_2SiH_2$

The substances taken for reaction were $(C_2H_5)_2Si(OC_2H_5)_2$ (41 g), LiH (13 g), and diisopentyl ether (50 ml). First a fraction of b.p. 54-56° was taken, and then a small amount of solvent came over. Fractionation through a 35-plate column yielded 7.7 ml (25%) of diethylsilane, b.p. 55.3° (757.5 mm); d_4^{20} 0.6843; n_D^{20} 1.3915. The literature [18] gives: b.p. 56° (741 mm); d_4^{20} 0.6843; n_D^{20} 1.3921.

SUMMARY

1. It has been shown for the first time that reduction by means of lithium hydride can be successfully extended to alkylhalosilanes and other classes of organosilicon compounds (alkenylhalosilanes, halo(haloalkyl)silanes; alkylethoxsilanes), and in the last case reduction proceeds selectively, without affecting the halogen of the haloalkyl group.

2. It has been shown that diallylsilane undergoes thiocyanation in almost theoretical yield, and that allylsilane combines with HCl in accordance with Markovnikov's rule.

3. The results provide data that characterize the dependence of the freezing points of some silanes on their structure. It has been shown also that the value of the refraction for the Si-C bond is determined by the radical containing the carbon attached to silicon. In particular, for allyl attached to silicon this value should be taken as 2.68 ml/mole.

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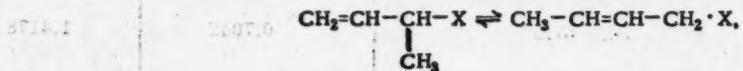
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SYNTHESIS AND PROPERTIES OF (1-METHYLALLYL)- AND 2-BUTENYL-SILANES

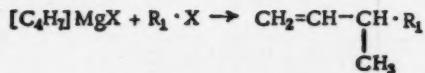
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UDC 547.553.2.4

Unsaturated sila-hydrocarbons, being convenient starting materials for the synthesis of various derivatives and the preparation of polymers, are attracting much attention. The syntheses and properties have been described of vinyl- and allyl-silanes [1], (2-methylallyl)silanes, and other unsaturated silanes [2]. The synthesis of (1-methylallyl)- and 2-butenyl-silanes by the Grignard-Wurtz method with the aid of 1-halo-2-butenes is associated with the necessity for the investigation of the allyl rearrangement of the latter:



for it cannot be predicted whether the process will be subject to exactly the same rules as those observed in the synthesis of hydrocarbons [3]. The most important of these rules is that the reaction will proceed by the scheme



(1)

i.e., mainly in the direction of secondary forms, when the halogen compound capable of rearrangement is applied in the form R·MgX, but, on the contrary, mainly in the direction of the formation of primary forms when the halogen compound capable of rearrangement is applied in the form RX, i.e., according to the scheme



(2)

We have accordingly carried out, on the one hand, reactions of $[\text{C}_4\text{H}_7]\text{MgBr}$ with $(\text{C}_2\text{H}_5)_3\text{SiCl}$, $\text{CH}_3\text{SiHCl}_2$ and SiCl_4 and, on the other hand, the reaction of $(\text{CH}_3)_3\text{SiCH}_2\text{MgCl}$ with $[\text{C}_4\text{H}_7]\text{Br}$. It was found that in all cases these same rules were obeyed. In the establishment of the main directions of these reactions much help was obtained from the application of Raman spectra.

Since it was not found possible to separate the mixture of (1-methylallyl)- and 2-butenyl-silanes obtained by reaction of $[\text{C}_4\text{H}_7]\text{MgBr}$ with $(\text{C}_2\text{H}_5)_3\text{SiCl}$ by fractionation through a column owing to the closeness of their boiling points, we decided to obtain an idea of the composition of this mixture from a study of Raman spectra. A comparison of the spectrum of the product of the hydrogenation of this mixture with that of authentic butyltriethylsilane showed that the amount of the latter in this product did not exceed 10% so that in this case the reaction went mainly in accordance with Equation 1.

The unsaturated sila-hydrocarbon formed by reaction of $(\text{CH}_3)_3\text{SiCH}_2\text{MgCl}$ with $[\text{C}_4\text{H}_7]\text{Br}$ gave a frequency of 1669 cm^{-1} and only traces of the frequencies 3000 cm^{-1} and 3078 cm^{-1} characteristic for a double bond at the end of the chain. This indicates that here the main reaction product is $(\text{CH}_3)_3\text{Si}-\text{CH}_2-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_3$, i.e., the reaction proceeds in accordance with Equation 2.

When 2-butenylmagnesium bromide was treated with SiCl_4 and with $\text{CH}_3\text{SiHCl}_2$, chloro(1-methylallyl)silanes again predominated in the products. For the determination of the ratio of the 1-methylallyl and 2-butenyl compounds it was found to be expedient to reduce the halogens with lithium hydride, since this yielded isomers having a greater difference in boiling point. At the same time, this reduction permitted the synthesis of the silicon analogs of 3-methyl-1-butene, 2-pentene, and 3-methyl-1-pentene, having in each case one carbon atom replaced by silicon.

Among the chemical properties of this new type of alkenylsilanes (having hydrogen attached to silicon) is their ability to undergo thiocyanation, and the thiocyanogen numbers are only slightly higher than the calculated values when dilute solutions are used. The physical properties of these unsaturated sila-hydrocarbons are shown in juxtaposition with those of the corresponding olefins in the table.

Apart from the substances shown in the table, we have prepared and characterized the following: 1) triethyl-(1-methylallyl)silane $(\text{C}_2\text{H}_5)_3\text{Si}-\text{CH}_3-\text{CH}-\text{CH}=\text{CH}_2$; 2) trichloro(1-methylallyl)silane $\text{Cl}_3\text{Si}-\text{CH}_3-\text{CH}-\text{CH}=\text{CH}_2$; 3) trimethyl-3-pentenylsilane $(\text{CH}_3)_3\text{Si}-\text{CH}_2-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_3$; 4) sec-butyltriethylsilane $(\text{C}_2\text{H}_5)_3\text{Si}-\text{CH}_2-\text{CH}_2-\text{CH}_3$. The

CH₃

Physical Properties of Olefins and Their Silicon Analogs

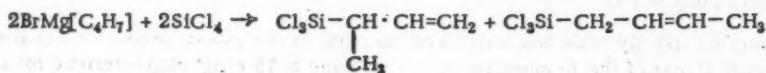
Compound	B.p. in °C (p in mm Hg)	d_4^{20}	n_D^{20}
$\begin{array}{c} \text{H}_3\text{C}-\text{CH}-\text{CH}=\text{CH}_2 \\ \\ \text{CH}_3 \end{array}$	36.5	0.6340	1.3677
3-Methyl-1-butene	20.1		
$\begin{array}{c} \text{H}_3\text{Si}-\text{CH}-\text{CH}=\text{CH}_2 \\ \\ \text{CH}_3 \end{array}$	43 (750)	0.6846	1.4050
(1-Methylallyl)silane			
$\begin{array}{c} \text{H}_3\text{C}-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_3 \\ \\ \text{2-Pentene} \end{array}$	36.5	0.6504	1.3793
$\begin{array}{c} \text{H}_3\text{Si}-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_3 \\ \\ \text{2-Butenylsilane} \end{array}$	56.0-57.5	0.7042	1.4178
$\begin{array}{c} \text{CH}_3-\text{CH}_2-\text{CH}-\text{CH}=\text{CH}_2 \\ \\ \text{CH}_3 \end{array}$			
3-Methyl-1-pentene	54	0.6700	1.3835
$\begin{array}{c} \text{CH}_3-\text{SiH}_2-\text{CH}-\text{CH}=\text{CH}_2 \\ \\ \text{CH}_3 \end{array}$			
Methyl(1-methylallyl)silane	70-71 (749)	0.7165	1.4162

sil-a-hydrocarbons given in the table were prepared by the reduction of the corresponding halosilanes with LiH; the sil-a-hydrocarbon No. 4 was prepared by reduction of No. 1 with hydrogen in presence of Raney nickel.

It should be noted that, whereas $(\text{C}_2\text{H}_5)_3\text{SiCl}$ condensed with a Grignard reagent having an allyl-type radical with formation of sil-a-hydrocarbon No. 1 in 35% yield, the condensation of the same chloro compound under the same conditions with sec-butylmagnesium chloride did not go at all. $(\text{CH}_3)_3\text{Si}-\text{CH}_2\text{Cl}$ was prepared by the chlorination of CH_3SiCl_3 to give $\text{Cl}_3\text{SiCH}_2\text{Cl}$ and the reaction of the latter with CH_3MgI . It was found that, not only $(\text{CH}_3)_3\text{SiCH}_2\text{Cl}$ (50% yield), but also $(\text{CH}_3)_3\text{SiCH}_2\text{I}$ was formed in appreciable amount (25.6% yield). The formation of this iodo compound is probably to be explained by the reaction:



It is interesting to note also that the mixture of trichloro(1-methylallyl)- and 2-butenyltrichloro-silanes formed by the reaction



polymerizes fairly readily with heat (when distilled), possibly partly owing to the presence of dialkenylsilane impurities.

EXPERIMENTAL

$\text{C}_4\text{H}_7\text{Br}$. A mixture of 336 g of butadiene and 155 g of glacial acetic acid was saturated with HBr at -10° . The product was washed free from acid, dried, and fractionated; 563 g of the fraction of b.p. $85-102^\circ$ was obtained.

$(\text{C}_2\text{H}_5)_3\text{SiC}_4\text{H}_7$. To 14 g of Mg in 600 ml of ether 10 g of $\text{C}_4\text{H}_7\text{Br}$ was added to initiate reaction. A mixture of 62 g of $(\text{C}_2\text{H}_5)_3\text{SiCl}$ and 40 g of $\text{C}_4\text{H}_7\text{Br}$ was added over a period of 3 hours 30 minutes. The ether was distilled off, and the contents of the flask were heated for six hours in a boiling water bath. Decomposition with water followed by fractionation through a 35-plate column yielded 22 g (35%) of $(\text{C}_2\text{H}_5)_3\text{SiC}_4\text{H}_7$, b.p. $185-188^\circ$ (750 mm); d_4^{20} 0.7990; n_D^{20} 1.4504; found MR 57.33; calculated MR 57.59.

$(\text{C}_2\text{H}_5)_3\text{SiC}_4\text{H}_2$. With the object of determining its structure $(\text{C}_2\text{H}_5)_3\text{SiC}_4\text{H}_7$ (17.8 g) was hydrogenated in a 150-ml autoclave in presence of Raney nickel at 180° and initial hydrogen pressure of 80 atm. The hydrogenation product, isolated with the aid of a 35-plate column, had b.p. $190.5-191.5^\circ$ (748.3 mm); d_4^{20} 0.7848; n_D^{20} 1.4383; found MR 57.68; calculated MR 58.06.

Found %: C 70.49; H 14.15; Si 15.55
(C_2H_5)₃SiC₄H₉. Calculated %: C 69.68; H 14.04; Si 16.28

For the purpose of the Raman analysis the synthesis of (C_2H_5)₃Si(*n*-C₄H₉) was repeated, the properties of which, according to the literature [4], are b.p. 192°; d_4^{20} 0.7786; n_D^{20} 1.4348. Our preparation had b.p. 190.5° (741.1 mm); d_4^{20} 0.7797; n_D^{20} 1.4350.

An attempt to prepare sec-butyltriethylsilane (which has not been synthesized previously) under the same conditions (i.e., condensation of (C_2H_5)₃SiCl with sec-butylmagnesium bromide, six hours, 80°) was not successful.

Raman spectra* were determined both for the hydrogenation product of (C_2H_5)₃SiC₄H₉, and for (C_2H_5)₃Si(*n*-C₄H₉).

1. *n*-Butyltriethylsilane:

cm^{-1} : 149 (3), 261 (4b), 303 (3), 333 (1), 515 (2), 550 (3), 569 (8), 638 (4b), 724 (4b), 752 (4b), 849 (4), 882 (6), 974 (5b), 1013 (4b), 1051 (4), 1079 (3), 1191 (4), 1236 (5b), 1292 (1), 1304 (3), 1345 (1), 1385 (3), 1418 (5), 1448 (3), 1467 (8).

2. Mixture of hydrogenation products:

cm^{-1} : 150 (3), 262 (3), 297 (3), 521 (2), 548 (2), 568 (8), 638 (3), 722 (2b), 850 (4), 880 (4), 910 (1), 973 (6), 1012 (4b), 1021 (2), 1050 (1), 1054 (1b), 1188 (2b), 1214 (1), 1236 (5), 1312 (2), 1382 (3), 1419 (4), 1452 (2), 1467 (7).

The spectrum of *n*-butyltriethylsilane contains the following characteristic frequencies: 1) for the normal chain in butyl: 1051 (4), 1079 (3), 1345 (1), 1448 (3); 2) for the ethyl radical attached to Si: 974 (5b), 1013 (4), 1236 (5b), 1467 (8), as noted previously [5]. The spectrum of the mixture, however, contains only frequencies characteristic for the ethyl radical: 973 (6), 1012 (4b), 1236 (5) and 1467 (7); the frequencies for the normal chain are either very weak or absent altogether. In their place there appear the lines 1021 (2), 1094 (1b), 1188 (2b) and 1452 (2), which may belong only to a branched butyl radical attached to silicon.

On the basis of these considerations it follows that the mixture contained mainly sec-butyltriethylsilane, and only a small amount (up to 10%) of *n*-butyltriethylsilane.

$Cl_3SiC_4H_7$. A mixture of 500 g of $SiCl_4$ and 200 g of C_4H_7Br was added at the rate of 95-100 drops per minute to 72 g of Mg in 1500 ml of ether. The ether was distilled off, and the mixture was heated for five hours in a water bath. The reaction product was filtered from the precipitate, and the residual ether and excess of $SiCl_4$ were distilled off. As the reaction product had become very thick, indicating that polymerization was setting in, monomer was distilled off under reduced pressure (70 mm). A fraction (79 g) of b.p. 57-102° was obtained, and the residue was a thick mass of polymer. Fractionation of the fraction through a column (Fig. 1) yielded 47.8 g of main product, b.p. 137-138° (757.5 mm); d_4^{20} 1.2013; n_D^{20} 1.4524; found MR 42.60; calculated for $Cl_3SiC_4H_7$, MR 42.59.

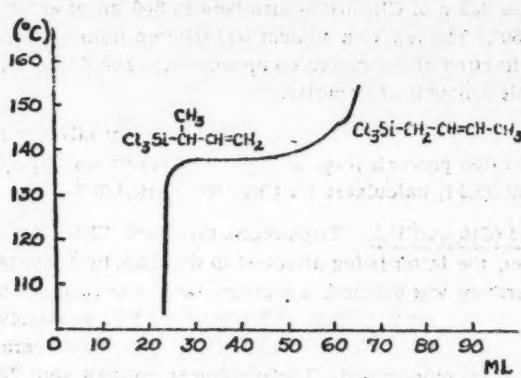
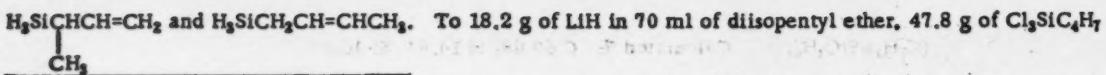


Fig. 1. Fractionation curve for the mixture of trichloro(1-methylallyl)- and 2-butetyltrichloro-silanes.

* The spectra were kindly determined by Yu. P. Egorov.



was added. The reduction was carried out in a still incorporating a small rectification column under the conditions described previously [6]. In the receiver, which was surrounded with a mixture of acetone and dry ice, 11.3 g of $\text{H}_3\text{SiC}_4\text{H}_7$ was collected, and this was fractionated through a 35-plate column (Fig. 2).

Fraction I, b.p. 43° (750 mm) was $\text{H}_3\text{Si}-\underset{\text{CH}_3}{\text{CH}}-\text{CH=CH}_2$; d_4^{20} 0.6846; n_D^{20} 1.4050; found MR 30.85; calculated for

$\text{H}_3\text{SiC}_4\text{H}_6$; MR 30.79.

Fraction II, b.p. 56.0-57.5° (752 mm) was $\text{H}_3\text{Si}-\text{CH}_2-\text{CH=CH-CH}_3$; d_4^{20} 0.7042; n_D^{20} 1.4178; found MR 30.83; calculated MR 30.79.

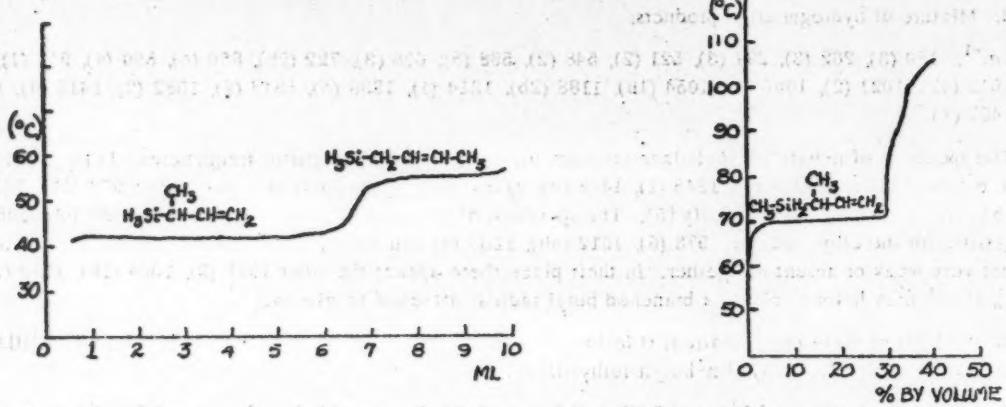


Fig. 2. Fractionation curve for the mixture of (1-methylallyl)- and 2-butenyl-silanes.

Fig. 3. Fractionation curve for methyl(1-methylallyl)silane.

$\text{CH}_3\text{SiH}(\text{Cl})(\text{C}_4\text{H}_7)$ and $\text{CH}_3\text{SiH}_2-\underset{\text{CH}_3}{\text{CH}}-\text{CH=CH}_2$. The Grignard reagent prepared from 40 g of Mg and 135 g of

$\text{C}_4\text{H}_7\text{Br}$ in 500 ml of ether was added to 206 g of $\text{CH}_3\text{SiHCl}_2$ dissolved in 300 ml of ether. The reaction was completed by heating in a water bath at 50°. The reaction product was filtered from the precipitate, and 118 g remained after removal of ether. The fraction of the chloro compound, b.p. 105.8-108.8°; d_4^{20} 0.8025; n_D^{20} 1.4259, was separated; it contained appreciable amounts of impurity.

The wide fraction of reaction products (47.5 g) was reduced with 15 g of LiH in a medium of diisopentyl ether. In the fractionation of the reduction products (Fig. 3) only one fraction was separated: b.p. 70.0-71.0° (749 mm); d_4^{20} 0.7165; n_D^{20} 1.4162; found MR 35.11; calculated for $\text{CH}_3-\text{SiH}_2\text{C}_4\text{H}_7$; MR 34.96.

$\text{Cl}_3\text{SiCH}_2\text{Cl}$, $(\text{CH}_3)_3\text{SiCH}_2\text{Cl}$, and $(\text{CH}_3)_3\text{SiCH}_2\text{I}$. Trichloromethylsilane Cl_3SiCH_3 was placed in a flask fitted with thermometer and reflux condenser, the latter being attached to the flask by a quartz tube having a porcelain filling. When the final boiling temperature was reached, a mercury lamp was switched on, and chlorine was passed into the reaction zone above the filling. During the whole of the reaction HCl was evolved. When the boiling point of the product attained 110°, the chlorination was discontinued. The products were fractionated through a column. Altogether 532 g of CH_3SiCl_3 was chlorinated. The substances isolated were 227 g of $\text{Cl}_3\text{SiCH}_2\text{Cl}$, 60 g of unchanged CH_3SiCl_3 , and 208 g of residue. The yield of $\text{Cl}_3\text{SiCH}_2\text{Cl}$ was 39% on the amount of CH_3SiCl_3 that reacted.

To 48.3 g of Mg in 600 ml of ether, 299.5 g of CH_3I was added, and to this Grignard reagent, 96 g of $\text{Cl}_3\text{SiCH}_2\text{Cl}$ was then added. The contents of the flask were heated in a boiling water bath for seven hours. The 73 g of reaction products remaining after removal of ether was fractionated through a 35-plate column (Fig. 4), and yielded:

Fraction I, b.p. 97.0° (752 mm) was $(\text{CH}_3)_3\text{Si-CH}_2\text{-Cl}$, 32 g; n_D^{20} 1.4172. For this chloro compound the literature [7] gives b.p. 97.1°; n_D^{20} 1.4180.

Fraction II, b.p. 139.5° was $(\text{CH}_3)_3\text{SiCH}_2\text{I}$, 28.5 g; n_D^{20} 1.4895. For this iodo compound the literature [7] gives b.p. 139.5° and n_D^{20} 1.4917.

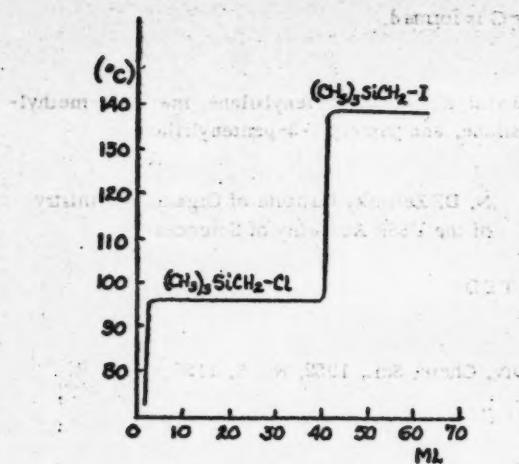


Fig. 4. Fractionation curve for the mixture of (chloromethyl)- and (iodomethyl)-trimethylsilanes.

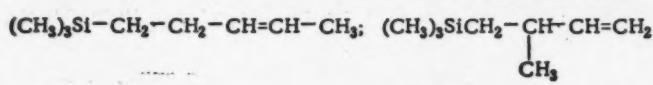
$(\text{CH}_3)_3\text{Si-CH}_2\text{-CH}_2\text{-CH=CH-CH}_3$. To $(\text{CH}_3)_3\text{SiCH}_2\text{MgCl}$, prepared from 32 g of $(\text{CH}_3)_3\text{SiCH}_2\text{Cl}$ and 6.5 g of Mg in 100 ml of ether, 36 g of $\text{C}_2\text{H}_5\text{Br}$ was added dropwise, under stirring.

Reaction was slow (slight rise in temperature). When the mixture was heated in a water bath, a very vigorous reaction set in, and part of the product was lost. The remaining 21.5 g was fractionated through a 35-plate column (Fig. 5), and two substances were isolated.

Fraction I was a sila-hydrocarbon of b.p. 139.8° (756.5 mm); d_4^{20} 0.7466; n_D^{20} 1.4235; found MR 48.58; calculated for $(\text{CH}_3)_3\text{SiCH}_2\text{C}_4\text{H}_7$ MR 48.35.

Found %: C 67.57; H 12.80; Si 19.56
 $(\text{CH}_3)_3\text{SiCH}_2\text{C}_4\text{H}_7$. Calculated %: C 67.53; H 12.75; Si 19.72

In the Raman spectrum of the substance of b.p. 139.8°, the frequency 1669 (8) was found, and only traces of the frequencies 1642 (2), 3000 (2), 3078 (1), and others. According to a previous investigation by Egorov [2, 5], the frequencies 1642 (2), 3000 (2), and 3078 (1) correspond to II (below), the content of this form being not greater than 5% judging from the intensities. The frequency 1669 (8) corresponds to I, which greatly predominates in the fraction, its content being about 95%.



(I)

(II)

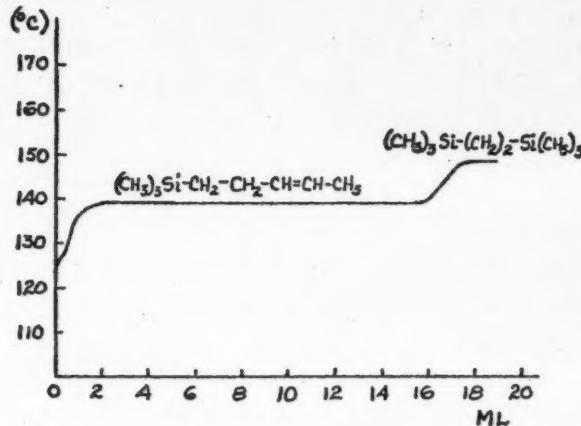


Fig. 5. Fractionation curve for the mixture of reaction products from $(\text{CH}_3)_3\text{SiCH}_2\text{MgCl}$ and $[\text{C}_4\text{H}_7]\text{Br}$.

Fraction II, b.p. 150°, was $(\text{CH}_3)_3\text{Si-CH}_2\text{-CH}_2\text{-Si}(\text{CH}_3)_3$; d_4^{20} 0.7566; n_D^{20} 1.4200; found MR 58.33; calculated for $(\text{CH}_3)_3\text{SiCH}_2\text{CH}_2\text{Si}(\text{CH}_3)_3$; MR 58.43. For this sila-hydrocarbon, the literature [8] gives b.p. 150-151°; d_4^{20} 0.7536; n_D^{20} 1.4204.

SUMMARY

1. It has been shown that in the Grignard-Wurtz synthesis of alkenylsilanes from 1-bromo-2-butenes, the latter undergo the same type of allyl rearrangement as in the synthesis of hydrocarbons, i.e., in the condensation of $\text{R}\cdot\text{MgX}$

(R = 2-butenyl) with R_1X ($R_1 = -Si-X$), (1-methylallyl)silanes $\begin{array}{c} >Si-C-C=C \\ | \\ C \end{array}$ are formed. When $R-X$ is condensed with R_1MgX ($R_1 = -Si-CH_2MgX$), a 3-pentenylsilane $\begin{array}{c} >Si-C-C-C=C-C \\ | \\ C \end{array}$ is formed.

2. Silicon analogs of olefins have been synthesized: (1-methylallyl)silane, 2-butenylsilane, methyl(1-methylallyl)silane, trichloro(1-methylallyl)silane, triethyl(1-methylallyl)silane, and trimethyl-3-pentenylsilane.

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* See Consultants Bureau Translation, page 989.

on repeated hydrogenation hydrogen uptake is small enough that this is regarded to indicate a skeletal iron catalyst. In 30 g of the aluminum was incorporated as a carrier and to ensure stimuli. A 1500 rpm shaker was used to stir the reaction mixture.

ACTIVITY OF A SKELETAL IRON CATALYST IN HYDROGENATION REACTIONS

L. Kh. Freidlina, K. G. Rudneva, and A. S. Sultanov

An iron catalyst prepared by the reduction of ferric oxide at 400-500° is of low activity for hydrogenation reactions [1]. Hydrogenation of acetylene in presence of this catalyst begins at 180°; it yields a mixture of hydrocarbons and is accompanied by the deposition of a carbonaceous film on the catalyst.

The first attempt to prepare a more active iron catalyst from an alloy was unsuccessful. Dupont and Piganiol [2] found that a skeletal iron catalyst prepared by the leaching of an iron-aluminum alloy was quite inactive. Paul and Hilly [3] showed that iron prepared by the leaching of an iron-aluminum alloy (20:80) at 80-90° catalyzed the hydrogenation of acetylenic compounds to ethylenic compounds by hydrogen at 100° under a pressure of 50 atm; but the catalyst was inactive for the hydrogenation of ethylenic compounds, nitriles, and compounds containing carbonyl and nitro groups.

The impression is formed that skeletal iron catalysts differ greatly in activity from skeletal nickel catalysts. We, however, have established [4] that the activity of a skeletal iron catalyst, like that of a nickel catalyst, is associated with the presence of hydrogen within it, i.e., the nature of the activity is similar. We showed also that an iron catalyst is more readily stripped of hydrogen and deactivated than a nickel catalyst. This suggested to us that the activity of a skeletal iron catalyst should be studied at a lower temperature, at which its active surface would be more stable. Our experiments have shown that this catalyst does, in fact, have a fairly high activity, and it can be used in much the same way as the nickel catalyst for the hydrogenation of many organic compounds at room temperature and normal pressure.

EXPERIMENTAL

Preparation of the Catalyst

An iron-aluminum alloy was prepared by Kurnakov's method [5] in a high-frequency furnace. Filings of Armco iron were added to melted aluminum contained in a porcelain crucible under a layer of slag. As a flux, a mixture of equal parts by weight of sodium and potassium chlorides was used, and during the alloying process, to reduce the volatility of the halides and avoid exposure of the metal, barium chloride was added. On account of the great difference in specific gravity between iron and aluminum, the mass was carefully mixed during the melting with a porcelain rod. When a homogeneous mixture had been obtained, the crucible was taken out of the furnace, and the melt was poured out onto an iron tray. When it had cooled to about 600°, the alloy was doused with cold water, and was then regarded as ready.

The alloy, in the form of a finely ground powder, was introduced in a current of hydrogen, into a 20% solution of sodium hydroxide at 60°. The temperature of the reaction mixture was maintained at not above 80° throughout the addition of the alloy. The resulting catalyst was cooled to room temperature and washed with distilled water until there was no reaction to phenolphthalein. The operations of cooling and washing were also carried out in a current of hydrogen. The catalyst was stored under a layer of absolute alcohol.

Hydrogenation of Various Organic Compounds in Presence of Skeletal Iron Catalyst at 20° (weight of catalyst: 1 g)

Substance hydrogenated	Amt. taken for reaction (g)	Hydrogen consumed (ml)	Degree of conversion (%)
Eugenol.....	0.3093	40.2	95
Phenyl vinyl ether.....	0.2495	46.7	100
Methyl methacrylate.....	0.3252	69.2	95
Styrene.....	0.2273	49.6	100
2-Methyl-5-hexen-3-yn-2-ol	0.1385	82.2	97
2-Butyne-1,4-diol.....	0.2174	112.0	99
Mesityl oxide.....	0.1755	39.7	98

Experimental Conditions

In all experiments the same sample of skeletal iron catalyst was used; it was prepared by the leaching of an alloy containing 66% of aluminum. The hydrogenation was carried out at 20° in a hydrogenation flask, 150 mm in length and 30 mm in diameter. The sweep of the shake was 10.5 cm, and the rate of shaking was not less than 700 oscillations per minute. These conditions were such as to ensure that the reaction occurred in the kinetic region. A mixture of 1 g of catalyst and 10 ml of alcohol was introduced into the

flask in a current of hydrogen, and was then given fifteen minutes to enable complete saturation with hydrogen to occur. A definite amount of the substance to be hydrogenated was then introduced in 5-10 ml of solvent, the shaker motor was switched on, and the rate of absorption of hydrogen was determined.

Activity of Skeletal Iron Catalyst

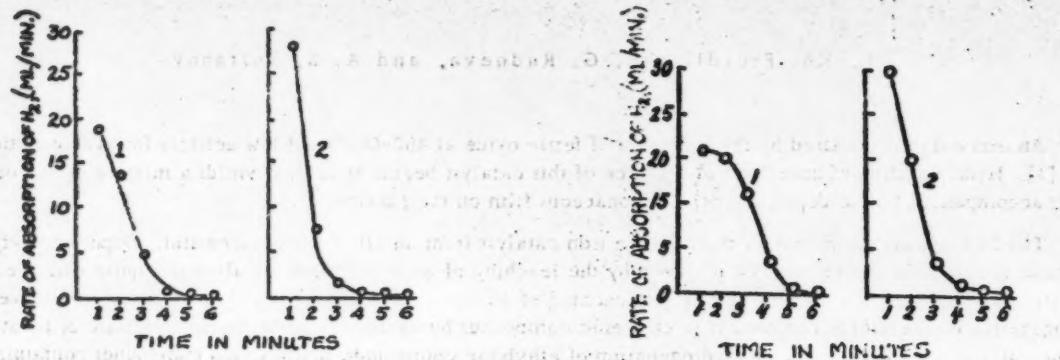


Fig. 1. Rate of hydrogenation of 0.3093 g of eugenol in alcohol at 20° in presence of 1 g of catalyst: 1) skeletal iron; 2) skeletal nickel.

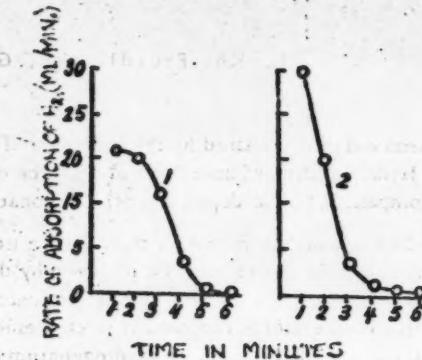


Fig. 2. Rate of hydrogenation of 0.2495 g of phenyl vinyl ether in alcohol at 20° in presence of 1 g of catalyst: 1) skeletal iron; 2) skeletal nickel.

Activity of Skeletal Iron Catalyst

For comparison purposes, in conjunction with the iron-catalyst experiments, studies were made of the activity of skeletal nickel catalyst in the same reactions and under analogous conditions. The nickel catalyst used was obtained by leaching a 50% Ni-Al alloy with 20% caustic soda at 105° for two hours. The relative activities of the iron and nickel catalysts were characterized by a comparison of the graphs showing the variation of the rate of hydrogen absorption with time for the hydrogenation of a definite weight of substance. The results of the experiments are given in the table and in Figures 1-9. The volume of hydrogen is always reduced to standard conditions.

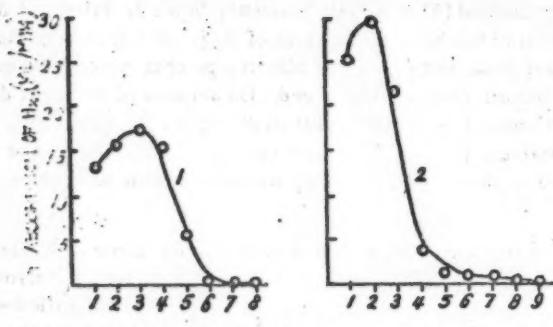


Fig. 3. Rate of hydrogenation of methyl methacrylate in alcohol at 20° in presence of 1 g of catalyst: 1) skeletal iron, 0.3252 g of ester; 2) skeletal nickel, 0.4028 g of ester.

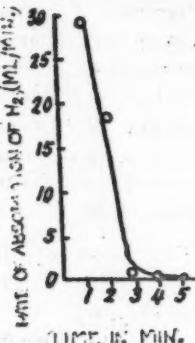


Fig. 4. Rate of hydrogenation of 0.2273 g of styrene in dioxane at 20° in presence of 1 g of skeletal iron catalyst.

Hydrogenation of Compounds Containing an Ethylene Bond

Figures 1, 2, 3, and 4 show the curves for the change in the rate of hydrogen absorption with time for the hydrogenation of four different compounds containing a double bond. It follows from the curves that eugenol, phenyl vinyl ether, methyl methacrylate, and styrene are hydrogenated rapidly, thus indicating the high activity of skeletal iron catalyst at 20° and normal pressure. The degree of hydrogenation of these compounds attains 95-100% of the theoretical value, and hydrogenation is complete in a few minutes. A comparison shows that the activity of an iron catalyst is quite of the same order as that of a skeletal nickel catalyst.

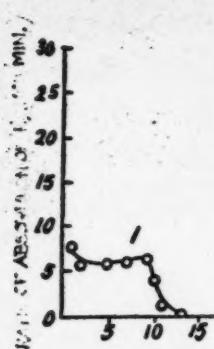


Fig. 5. Rate of hydrogenation of 0.0996 g of 2-methyl-3-butyn-2-ol in alcohol at 20° in presence of 1 g of catalyst: 1) skeletal iron; 2) skeletal nickel.

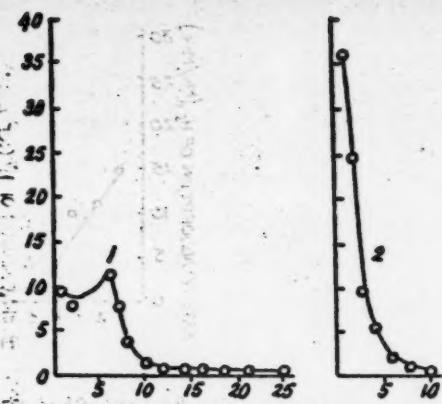


Fig. 6. Rate of hydrogenation of 0.1385 g of 2-methyl-5-hexen-3-yn-2-ol in alcohol at 20° in presence of 1 g of catalyst: 1) skeletal iron; 2) skeletal nickel.

Hydrogenation of Compounds Containing a Triple Bond

It will be seen from Figures 5, 6, and 7 that, unlike the curves for the nickel catalyst, those for the rate of hydrogenation in presence of skeletal iron have complicated forms. On the curve for the hydrogenation of 2-methyl-3-butyn-2-ol (Fig. 5), at the point corresponding approximately to 50% consumption of hydrogen, there is a break in the curve indicating a sharp fall in the rate of the process. The curve for the hydrogenation of 2-methyl-5-hexen-3-yn-2-ol is similar in character (Fig. 6). On this curve the break occurs at a point corresponding to two-thirds of the total amount of hydrogen consumed. The curve for the hydrogenation of 2-butyne-1,4-diol is still more complex in form (Fig. 7); almost 50% of the hydrogen is absorbed at a constant rate, and there is then a definite rise in the rate of the process, which is followed finally by a fall.

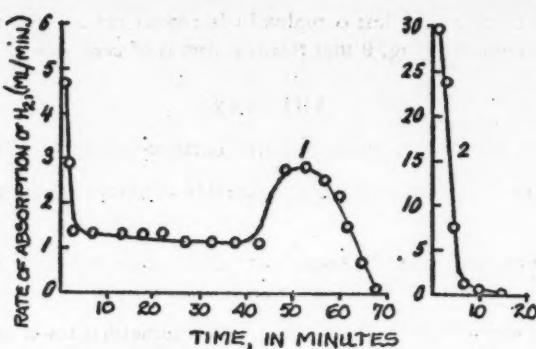


Fig. 7. Rate of hydrogenation of 0.2174 g of 2-butyne-1,4-diol in alcohol at 20° in presence of 1 g of catalyst: 1) skeletal iron; 2) skeletal nickel.

It follows from these results that for the hydrogenation of triple bonds skeletal iron catalyst again has a considerable activity, although it is somewhat lower than in the case of double bonds. There is a particularly marked difference in the rates of the process in presence of iron and nickel catalysts in the case of the hydrogenation of 2-butyne-1,4-diol.

Hydrogenation of Carbonyl Compounds

In the hydrogenation of mesityl oxide, the total consumption of hydrogen did not exceed the amount required for the hydrogenation of the double bond; it would appear that, under these conditions, the carbonyl group is not hydrogenated (Fig. 8).

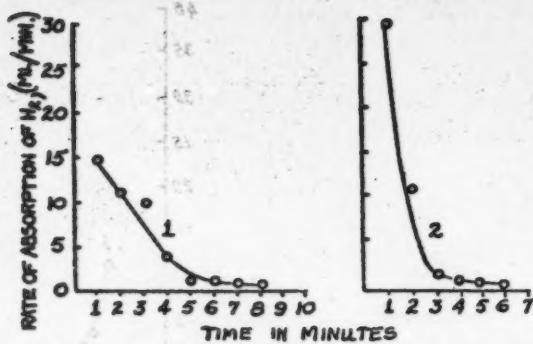


Fig. 8. Rate of hydrogenation of 0.1755 g of mesityl oxide in alcohol at 20° in presence of 1 g of catalyst: 1) skeletal iron; 2) skeletal nickel.

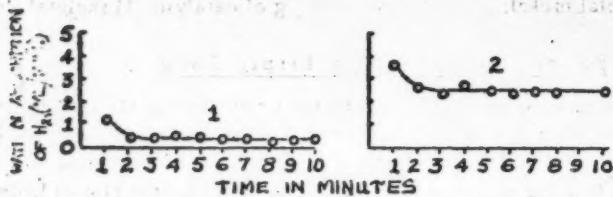


Fig. 9. Rate of hydrogenation of 0.1494 g of 2-butanone in alcohol at 20° in presence of 1 g of catalyst: 1) skeletal iron; 2) skeletal nickel.

In 2-butanone, a compound containing a less complex hydrocarbon radical, the carbonyl group is hydrogenated, although at a low rate. It will be seen from Fig. 9 that this reaction is of zero order.

SUMMARY

1. A study has been made of the activity of skeletal iron catalyst in hydrogenation reactions.
2. It has been established that this catalyst has a considerable activity in hydrogenation reactions at 20° and normal pressure.
3. The activity of an iron catalyst for the hydrogenation of an ethylene bond is two to three times less than that of a skeletal nickel catalyst.
4. Compounds containing a triple bond are hydrogenated at a somewhat lower rate than compounds containing an ethylene bond. A carbonyl group is hydrogenated still more slowly.

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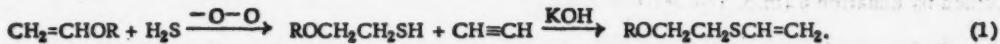
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SYNTHESIS OF SULFUR COMPOUNDS BY THE AID OF VINYL ETHERS AND ACETYLENE

COMMUNICATION 9. SYNTHESIS AND CERTAIN PROPERTIES OF 2-ALKOXYETHYL VINYL SULFIDES

M. F. Shostakovskiy and E. N. Prilezhaeva

Addition of hydrogen sulfide to alkyl vinyl ethers in the direction contrary to that required by Markovnikov's rule [1, 2] results in the synthesis of a homologous series of 2-alkoxyethanethiols, which have, therefore, become readily accessible substances. By the action of acetylene on these thiols in presence of caustic potash powder, we have readily prepared the corresponding 2-alkoxyethyl vinyl sulfides, and have thus effected the transition from vinyl ethers to these vinyl sulfides.



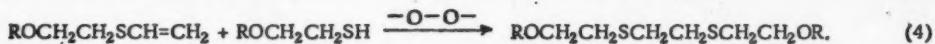
Some unsubstituted vinyl sulfides have been described previously in patent specifications by Reppe and co-workers [3], who prepared them by the vinylation of thiols with acetylene diluted with nitrogen. In Soviet literature, an attempt has been described [4] to apply the method of vinylation developed for alcohols by Favorsky and Shostakovskiy [5] (vinylation with acetylene without dilution with inert gases) to the synthesis of isopentyl vinyl sulfide. The author, however, first converted the 3-methylbutanethiol into its potassium derivative, which naturally yielded considerable amounts of diisopentyl sulfide, thus reducing the yield of the vinyl sulfide.

We have previously shown [6] that by slight modification of the Favorsky-Shostakovskiy method it is possible to synthesize ethyl vinyl sulfide from ethanethiol in fairly good yield (about 50%), the only by-product being 1,2-bis(ethylthio)ethane:



The extension of the use of these reaction conditions to 2-alkoxyethanethiols, which are of lower volatility and higher molecular weight, leads to the synthesis of the corresponding vinyl sulfides in 70-80% yield.

The secondary reaction, the formation of disulfides (Equation 4), is suppressed owing to the appreciable excess of acetylene (1.5-1.7 moles per mole of thiol) and the maintenance of almost complete absence of oxygen in the reaction medium (see experimental part)



2-Alkoxyethyl vinyl sulfides are fairly viscous liquids having odors that are somewhat improved by the presence of the alkoxy group in the molecule. The higher the weight of the radical in the alkoxy group, the more it suppresses the odor of the sulfur-containing residue; 2-octyloxyethyl vinyl sulfide has an odor similar to that of octyl alcohol.

In the study of the chemical properties of 2-alkoxyethyl vinyl sulfides, there were immediate indications of their essential difference from vinyl ethers. For example, these vinyl sulfides slowly polymerized in presence of air and diffuse light with formation of colorless, viscous liquid polymers. Chlorides, such as FeCl_3 and SnCl_2 , which catalyze the polymerization of vinyl ethers [7], did not promote any appreciable polymerization in 2-butoxyethyl vinyl sulfide, either in the cold, or when heated in a sealed tube at 100° for 24 hours. On the other hand, according to preliminary trials, the presence of this sulfide suppresses the polymerization of butyl vinyl ether in presence of FeCl_3 to a considerable extent.

When 2-butoxyethyl vinyl sulfide and 2-butoxyethanethiol are brought together in the air, 1,2-bis(2-butoxyethylthio)ethane is formed quantitatively in accordance with Equation 4. Here the addition of thiol occurs exclusively contrary to Markovnikov's rule, which is different from the behavior of vinyl ethers: in presence of air these give mixtures of abnormal and normal addition products with thiols [8].

Introduction of sulfur in place of oxygen in the molecule of a vinyl ether evidently reduces the tendency for its double bond to undergo reactions having an ionic character and increases the probability of reactions of the free-radical type.

The action of mercuric chloride on 2-alkoxyethyl vinyl sulfides in an absolute ether medium results in the formation of a noncrystallizing viscous complex salt. A completely different reaction occurs in ethanol solution. In this case the thiol residue separates quantitatively as the mercurichloride, an equivalent amount of HCl is liberated, and an acetal is evidently formed in accord with the following overall equation:



When an aqueous solution of mercuric chloride is used, acetaldehyde is formed. Hence, the alkylthio group in vinyl sulfides is split off just as readily by the action of mercuric chloride as in monothioacetals [9] and mercatals [9, 10]; the presence of alcohol or water is, however, necessary. Consideration of the mechanism of this process will be given later on the basis of supplementary experimental data. The reaction goes almost quantitatively; the titration of the hydrochloric acid that separates with 0.1 N NaOH in presence of Methyl orange can be used for the quantitative determination of the vinyl sulfide.

It is interesting that Davis and Oxford [11] obtained what they considered to be a complex salt of 2-ethoxyethyl vinyl sulfide by the action of mercuric chloride; it melted at 152-153°, but "did not give satisfactory analytical figures". The substance that they had actually obtained was 2-ethoxyethylthiomercury chloride $\text{C}_2\text{H}_5\text{OCH}_2\text{CH}_2\text{SHgCl}$, formed by Equation 5 (m.p. 154.5-155.5°).

Hence, the reaction of vinyl sulfides with mercury salts is again essentially different from the corresponding reaction of vinyl ethers. As Nesmeyanov, Lutsenko, and Vereshchagina showed [12], mercury salts add at the double bond of a vinyl ether, the final product being mercurated acetaldehyde. In vinyl sulfides the action of the mercury salt is apparently directed to the second reaction center, the sulfur atom.

EXPERIMENTAL

Synthesis of 2-Alkoxyethyl Vinyl Sulfides

The preparation of the thiols used in the synthesis of 2-alkoxyethyl vinyl sulfides has been described in previous communications [1, 2]. These thiols had the following physical constants (Table 1):

TABLE 1

Properties of 2-Alkoxyethanethiols $\text{ROCH}_2\text{CH}_2\text{SH}$

R	B.p. in °C (p in mm Hg)	n_D^{20}	d_4^{20}
C_2H_5	126-128 (760)	1.4456	0.9412
p- C_3H_7	64 (40)	1.4478	0.9227
1- C_3H_7	56.1-56.4 (44)	1.4424	0.9136
p- C_4H_9	48 (6)	1.4488	0.9111
1- C_4H_9	45.2-45.5 (9)	1.4444	0.9038
1- C_5H_{11}	53.9-54.5 (6)	1.4489	0.9028
p- C_8H_{17}	103 (4.5)	1.4556	0.8906
C_6H_{11} (cyclohexyl)	73-73.5 (45)	1.4864	0.9938

All vinylation reactions were carried out in horizontal stainless steel rotating autoclaves. The thiols were freshly distilled for the vinylations. In all experiments the amount of KOH powder taken was 5% on the weight of the thiol. The weight of thiol was chosen so that there would be a considerable excess of acetylene when the autoclave was filled only once with this gas during the experiment. The KOH and thiol were introduced into the autoclave, and the gases present were displaced by acetylene. Acetylene was then passed into the autoclave, and heating was commenced. The temperature was maintained within the range 135-150°, for 1.2-2.0 hours for small loads (0.15-liter autoclave) and 2-2.5 hours for large loads (0.5-2.5-liter autoclaves). After cooling, the reaction mixture was left until the next day. The excess of acetylene was liberated, and the reaction products were washed into a flask with a small amount of dry ether. The vinyl sulfides were isolated by vacuum distillation: in the first fractionation they came over within a range of 2-3°, and when redistilled their constants were unaffected. The yields of products, as obtained in the first fractionation, are given in Table 2. In all of the experiments there were very small amounts of dark-colored residue, which were not investigated in the experiments with small amounts of starting materials. Experiments on the vinylation of larger amounts of 2-butoxyethanethiol (Expts. No. 6 and 7) showed that, in addition to resin, these residues contained some disulfides, formed by Equation 4.

It will be seen from Table 2 that for a good yield an excess of acetylene is essential (1.5-1.8 moles per mole of thiol). The change from small amounts of thiol (Expts. No. 1-5 and 8-13) to large amounts (Expts. No. 6 and 7) is naturally accompanied by increase in the yield of vinyl sulfide (from 60-70% to 80-83%).

The results in Table 2 indicate how greatly any variation from the established procedure can affect the yield of sulfide. In Expt. No. 3, for example, the air in the autoclave was not displaced by acetylene before the vinylation, and this resulted in a great reduction in the yield of vinyl sulfide (to 53%) and in a rise in the amount of high-boiling residue. In this experiment, distillation of the residue yielded 1.8 g of a substance of b.p. 160-166° (6 mm).

TABLE 2

Conditions of the Synthesis of the Sulfides $\text{ROCH}_2\text{CH}_2\text{SCH}=\text{CH}_2$ from the Thiols $\text{ROCH}_2\text{CH}_2\text{SH}$

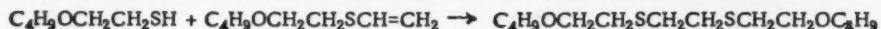
Expt. No.	R	Amt. of thiol taken (g)	Capacity of autoclave (liters)	C_2H_2 (moles per mole of thiol)	Duration of heating (hr)	Yield of sulfide (%)	Weight of resinous residue (g)
1	C_2H_5	8.0	0.15	1.4	1.0	60.0	~2
2	C_2H_5	6.5	0.15	1.7	2.0	71.6	<1
3	p- C_3H_7	9.5	0.15	1.7	1.5	52.8	3
4	p- C_3H_7	9.5	0.15	1.3	1.5	68.1	<1
5	1- C_3H_7	9.5	0.15	1.7	1.2	73.6	<1
6	p- C_4H_9	30.0	0.5	1.8	2.5	80.5	2.7
7	p- C_4H_9	154.5	2.5	1.6	2.5	83.2	10.4
8	1- C_4H_9	11.	0.15	1.6	2.0	71.3	<1
9	1- C_5H_{11}	12.0	0.15	1.0	1.0	61.7	2
10	1- C_5H_{11}	7.3	0.15	1.7	2.0	81.1	<1
11	p- C_6H_{17}	15.3	0.15	1.7	1.5	73.6	<1
12	C_6H_{11} (cyclohexyl)	11.2	0.15	1.3	2.0	41.4	3
13	C_6H_{11} (cyclohexyl)	9.8	0.15	1.7	1.5	70.1	~1

evidently the disulfide $\text{p-C}_3\text{H}_7\text{OCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{OC}_3\text{H}_7$ -p. In all of the other experiments the air was carefully displaced by acetylene.

In Expts. No. 1 and 9, the low yield is to be explained by the insufficiently long period of heating and by the inadequate amount of acetylene present in the reaction medium (particularly in Expt. No. 9). The removal of these defects greatly increased the yield (Expts. No. 2 and 10). In Expt. No. 12, the low yield is to be explained by the fact that during the vinylation the temperature of the reaction mixture was allowed to rise to 180° . In this case, in addition to the product indicated in the table, 1.4 g of cyclohexanol was obtained (b.p. $47.5-50^\circ$ (6 mm); n_D^{20} 1.4380; d_4^{20} 0.9478; the literature [13] gives b.p. 160.5° (758 mm); n_D^{20} 1.4350; d_4^{20} 0.9471). This alcohol was evidently formed by breakdown of the original thiol. In Expt. No. 13 standard reaction conditions were observed, and the yield of sulfide was not lower than for the other thiols. In this experiment no cyclohexanol was obtained.

2-Alkoxyethyl vinyl sulfides are colorless liquids that may be distilled under reduced pressure without decomposition or resinification; when stored in the air, they slowly polymerize with rise in refractive index. The physical properties and analyses of these sulfides are given in Table 3. The specific gravity and refractive index slowly fall as the alkoxy group becomes larger or more branched. The whole series of these substances has a small, but definite, systematic exaltation of molecular refraction (+ 0.2 to + 0.4).

Addition of 2-Butoxyethanethiol to 2-Butoxyethyl Vinyl Sulfide



The sulfide (62.5 g; b.p. $74-75^\circ/6$ mm) was mixed with the thiol (70.0 g; b.p. $48-49^\circ/6.5$ mm) in a conical flask (1.3 moles of the thiol to one mole of the sulfide). After ten minutes the temperature began to rise rapidly; it attained 75° , and then fell just as rapidly. The mixture was set aside overnight. Vacuum fractionation (3.1 mm) yielded the following fractions:

Fraction I, b.p. $39-41^\circ$, 16.0 g; n_D^{20} 1.4489;

Fraction II, b.p. $41-174^\circ$, 0.12 g;

Fraction III, b.p. $174-176^\circ$, 110.0 g; n_D^{20} 1.4870.

Fraction I was excess of thiol.

After refractionation, Fraction III came over completely at $175-175.5^\circ$ (3.2 mm) and had n_D^{20} 1.4869; d_4^{20} 0.9778; calculated MR 86.04; found MR 86.61.

Found %: C 57.31; 57.20; H 10.37, 10.31; S 21.76, 21.86

$\text{C}_{14}\text{H}_{30}\text{O}_2\text{S}_2$.

Calculated %: C 57.09; H 10.27; S 21.77

The product gave no red coloration with Methyl orange after addition of excess of an alcoholic solution of mercuric chloride. It may, therefore, be concluded that it consisted of the pure sulfide:

TABLE 3

Properties of 2-Alkoxyethyl Vinyl Sulfides $\text{ROCH}_2\text{CH}_2\text{SCH}=\text{CH}_2$

No.	R	B.P. in °C (p in mm Hg)	d_4^{20}	n_D^{20}	MR		Composition				calculated H%	S%
					found	calculated	C%	H%	S%	C%		
1	C_2H_5^*	59.5-60 (14)	0.9475	1.4760	39.38	39.12	54.08	9.27	24.06	54.50	9.14	24.25
2	$p\text{-C}_3\text{H}_7$	45 (3)	0.9309	1.4750	44.17	43.74	54.37	9.15	23.98	57.48	9.65	21.92
3	$i\text{-C}_3\text{H}_7$	51.6-51.8 (7)	0.9258	1.4684	43.94	43.74	57.64	9.72	21.66	57.48	—	—
4	$p\text{-C}_4\text{H}_9$	72.4-72.8 (5)	0.9232	1.4721	48.50	48.36	59.79	10.14	20.14	59.94	10.07	20.02
5	$i\text{-C}_4\text{H}_9$	69.5 (6.5)	0.9139	1.4678	48.68	48.36	59.68	10.09	20.18	—	—	20.02
6	$i\text{-C}_5\text{H}_{11}$	72.2-72.5 (4)	0.9115	1.4691	53.26	52.98	61.89	10.41	18.46	62.01	10.41	18.40
7	$p\text{-C}_6\text{H}_{17}$	106.6-107.1 (2)	0.9006	1.4709	67.12	66.83	61.86	10.43	18.24	—	—	14.82
8	C_6H_{11} (cyclohexyl)	98.5-99 (4)	0.9942	1.5025	55.38	55.39	64.36	9.68	17.26	64.47	9.74	17.21

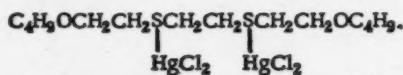
* According to the results of Davis and Oxford [1], 2-ethoxyethyl vinyl sulfide has b.p. 65° (8 mm) and d_4^{20} 0.9532. The nonagreement of these constants with ours is evidently to be explained by the fact that Davis and Oxford were dealing with an insufficiently pure substance, for they isolated this sulfide from a complex mixture obtained by the hydrolysis of bis(2-chloroethyl) sulfide with KOH in an aqueous-alcoholic medium. These authors state that the sulfide darkens with keeping; we did not observe this. No other sulfides of this series have been described in the literature.



and did not contain any of the isomeric mercaptal $CH_3CH(SCH_2CH_2OC_4H_9)_2$, which, as we in collaboration with Shapiro [9] have already shown, behaves like other mercaptals [10] and gives the mercurichloride of the thiol and HCl when treated with mercuric chloride.

Hence, the thiol adds to the vinyl sulfide entirely in the direction contrary to Markovnikov's rule (yield 95.8% on the amount of sulfide taken).

When the disulfide ($C_4H_9OCH_2CH_2SCH_2-$)₂ was treated with an equimolecular amount of mercuric chloride in ethanol, a noncrystallizing alcohol-insoluble oil was precipitated; it was not investigated further. After the addition of a considerable excess of ethanolic mercuric chloride (more than two moles per mole of sulfide), an oil was precipitated, and this gradually solidified when rubbed with a rod. Recrystallization from a small amount of boiling ethanol and drying in a vacuum desiccator yielded white crystals, m.p. 68.5-69°. Analysis indicated the formation of a complex salt with two molecules of mercuric chloride:



Found %: C 20.34; 20.29; H 3.66; 3.73

$C_{14}H_{30}O_2S_2 \cdot 2HgCl_2$. Calculated %: C 20.08; H 3.78

Reaction of 2-Alkoxyethyl Vinyl Sulfides with Mercuric Chloride in Ethanol Solution

A weighed amount of the vinyl sulfide was transferred from a small dropping bottle to a 50-ml flask having a ground-in stopper. A 20% solution of $HgCl_2$ in ethanol was then added from a buret in a two- to three-fold excess over that required by Equation 5. The mercurichloride began to be precipitated after 15-20 minutes. It was found

that it was necessary to leave the reaction mixture for one day in order to ensure completion of reaction. It was then titrated with 0.1 N NaOH with Methyl orange as indicator (20 ml of water was first added). The transition from the pink to the yellow color is fairly sharp. Completion of reaction is indicated by the nonreturn of the pink color of the indicator after the end of the titration. If the titration is performed within two or three hours of the mixing of the reactants, the color returns and the titration does not give quantitative results.

It will be seen from Table 4 that such a method of titration permits vinyl sulfides to be quantitatively determined in presence of other substances (so long as these do not react with HCl and do not yield HCl when treated with mercuric chloride). On the average, the results are accurate within 1%.

Table 5 shows the weights of precipitate and the melting points of the alkoxyethylthiomercury chlorides formed by the precipitation of weighed amounts of the corresponding sulfide with mercuric chloride. These melting points agree with those of the mercurichlorides obtained by us in collaboration with Shapiro from the corresponding 2-alkoxyethanethiols [1, 2]. There was no depression in mixture melting points of the mercurichlorides obtained by the two methods. The results in Tables 4 and 5 confirm that the reactions of vinyl sulfides with mercuric chloride in ethanol go quantitatively in accordance with Equation 5.

Decomposition of 2-Butoxyethyl Vinyl Sulfide with Mercuric Chloride in Aqueous Solution



A mixture of 15 g of mercuric chloride, 2.6 g of $BaCO_3$, and 20 ml of water was placed in a flask fitted with reflux condenser and tube for passage of gas, and 4.0 g of 2-butoxyethyl vinyl sulfide was added; the mixture became slightly warm. The mixture was heated at a gentle boil in a slow current of nitrogen for 40 minutes. The acetaldehyde liberated was trapped in two traps, filled with ethanol and cooled with snow and salt. Toward the end of the heating, the precipitate became slightly yellow. The contents of the traps, which smelled strongly of acetaldehyde, were transferred to a measuring flask, diluted with water, and titrated by Ripper's method [15]. The amount of acetaldehyde found by titration was 0.45 g, and the amount calculated theoretically was 1.1 g, so that we succeeded in trapping only 40-45% of the acetaldehyde.

TABLE 5

Melting Points and Yields of the Mercurichlorides $\text{ROCH}_2\text{CH}_2\text{SHgCl}$

R	Amt. of sulfide taken (g)	Yield of mercurichloride (g)*		M.p. of the mercurichloride (°C)**	
		found	calculated	from sulfide	from thiol [1, 2]
C_2H_5	0.6	1.86	1.55	154-155***	154.5-155.5
p- C_6H_5	0.8	1.85	1.94	138.5	137-137.5
i- C_3H_7	0.54	1.73	1.31	154-154.5	153-153.5
p- C_4H_9	0.41	1.02	0.94	136.5-137.5	137.5-138
i- C_4H_9	0.5	0.98	1.15	143.5	144-144.5
i- C_5H_{11}	0.66	1.85	1.45	126-127	126
p- C_6H_{17}	0.9	1.57	1.76	125-127	126
C_6H_{11} (cyclohexyl)	0.5	1.20	1.06	151	150.5

* The yield refers to the precipitate before recrystallization; it was filtered from the excess of mercuric chloride solution two or three days after the precipitation, washed with cold alcohol on a glass filter, and dried to constant weight in a vacuum desiccator.

** The melting points are those of the twice recrystallized mercurichlorides (from boiling ethanol). After a single recrystallization, the melting range was rather wide and an opaque liquid was formed.

*** This mercurichloride has been prepared previously from the corresponding thiol by Swallen and Boord [14] (m.p. 152-153.5°), and also, it would appear, from 2-ethoxyethyl vinyl sulfide by Davis and Oxford [11] (m.p. 152-153°).

Polymerization of 2-Butoxyethyl Vinyl Sulfide with Storage

When 2-butoxyethyl vinyl sulfide is stored, its refractive index slowly rises. For example, after being stored for 2.5 months in a flask with a ground-in stopper, the sulfide had n_D^{20} 1.4746, instead of the original value, 1.4721. Distillation of 16 g of this product yielded 14 g of the pure sulfide, b.p. 55° (2 mm) and n_D^{20} 1.4720. The residue was colorless and of the consistency of glycerol; it had n_D^{20} 1.5048 and weighed 1.9 g. In another case, the sulfide, after being stored for five months in a sealed tube, had n_D^{20} 1.4768. Distillation of 26.4 g yielded 21.6 g of monomeric sulfide, b.p. 62-63.5° (3 mm) and n_D^{20} 1.4721. The colorless viscous residue had n_D^{20} 1.5055 and weighed 4.0 g.

The polymers were transferred to a wide beaker and dried in a vacuum desiccator at 130-140° to constant weight; they became slightly yellow under this treatment.

Found %: C 59.83; 59.84; H 10.07, 10.10; S 20.04, 20.41
 $(\text{C}_4\text{H}_{16}\text{OS})_p$. Calculated %: C 59.92; H 10.07; S 20.02

The molecular weight of these polymers, determined by the cryoscopical method in benzene, was 2500-3000 (degree of polymerization about 20).

When 2-butoxyethyl vinyl sulfide that has been distilled in a current of nitrogen is stored in the dark in a sealed tube previously filled with nitrogen, no polymer formation is observed, even after six months. This vinyl sulfide, therefore, unlike vinyl ethers, tends to undergo slow polymerization under the action of light and oxygen.

All of the microanalyses for the present investigation and for those of the preceding communications [1, 2, 8, 9] were carried out in the Microanalysis Laboratory of the Institute of Organic Chemistry of the USSR Academy of Sciences by the method of simultaneous determination of C, H, and S developed in that laboratory by Korshun and Sheveleva [16].

SUMMARY

1. A method is given for the synthesis of 2-alkoxyethyl vinyl sulfides from 2-alkoxyethanethiols in 70-80% yield.
2. A method is proposed for the quantitative determination of vinyl sulfides; it is based on the decomposition reaction occurring in presence of mercuric chloride.
3. A study of some of the chemical properties of 2-alkoxyethyl vinyl sulfides shows that vinyl sulfides differ greatly from their oxygen analogs in their reactions.

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* See Consultants Bureau Translation, page 235.

** See Consultants Bureau Translation, page 245.

*** See Consultants Bureau Translation, page 325.

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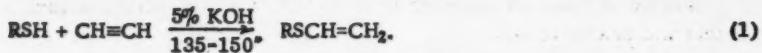
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SYNTHESIS OF SULFUR COMPOUNDS BY THE AID OF VINYL ETHERS AND ACETYLENE

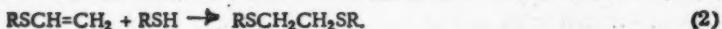
COMMUNICATION 10. SYNTHESIS AND CERTAIN REACTIONS OF ETHYL VINYL SULFIDE

M. F. Shostakovsky, E. N. Prilezhaeva, and N. I. Uvarova

It has been shown previously that a satisfactory method for the preparation of vinyl sulfides, including ethyl vinyl sulfide, is the vinylation of thiols under the reaction conditions of Favorsky and Shostakovsky [1, 2]:



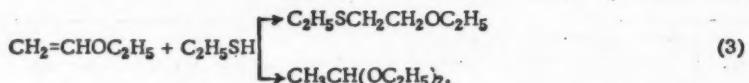
The vinylation of thiols must be effected in presence of a considerable excess of acetylene in order to reduce the probability of the occurrence of a secondary reaction between the alkyl vinyl sulfide formed and the thiol (by Equation 2):



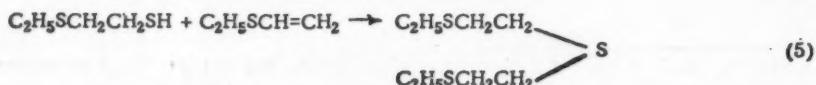
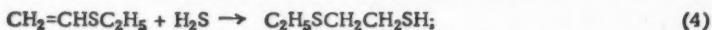
Ethyl vinyl sulfide has been synthesized also by the reaction of vinyl bromide with the alkali-metal derivatives of ethanethiol in alcoholic solution [3, 4] and by the dehydration of 2-mercaptopropanol, prepared by the action of ethylene oxide on ethanethiol [5]. By the reaction of hydrogen sulfide with acetylene in presence of polysulfide catalysts [6], a mixture of ethyl vinyl sulfide, ethanethiol, and 1,2-bis(ethylthio)ethane has been obtained. By the action of acetylene diluted with nitrogen on ethanethiol in presence of alkaline catalysts, Reppe [7, 8] and coworkers have obtained ethyl vinyl sulfide (Equation 1) and 1,2-bis(ethylthio)ethane (Equation 2) in the molar ratio of 2:3.

Some of the methods cited above are described only in the patent literature [5, 6, 7]; others give poor yields (about 20-25%) [3, 4].

The object of the present investigation was the study of the chemical transformations of ethyl vinyl sulfide, and also the improvement of the method of synthesis by the reaction of Favorsky and Shostakovsky. For this purpose we first studied the nature of the above-mentioned secondary process, the example taken being the reaction between ethanethiol and ethyl vinyl sulfide, which results in the formation of 1,2-bis(ethylthio)ethane (Equation 2). It was shown that, if ethanethiol and acetylene are brought together under vinylation conditions in the molar ratio 2:1, the disulfide is the only reaction product. Thus, in spite of Reppe's assertion [8], an alkaline catalyst cannot prevent reaction between the thiol and the vinyl sulfide. The experiment cited shows that this reaction is rapid and quantitative in presence of air or traces of oxygen, and is suppressed by the antioxidant hydroquinone, i.e., shows the typical properties of free-radical processes. Addition of hydroquinone to the reaction mixture does in fact permit the yield of disulfide to be greatly reduced, and it enables the vinylation to be carried out by means of repeated doses of acetylene (as in the case of alcohols). In presence of air, 1,2-bis(ethylthio)ethane is the sole product of the reaction of ethyl vinyl sulfide with ethanethiol, whereas under these conditions ethyl vinyl ether gives a mixture of products of addition according to and contrary to Markovnikov's rule [9]:

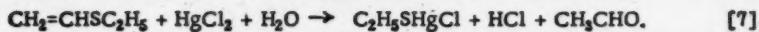
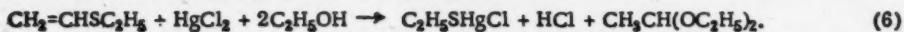


The nature of the reaction between ethanethiol and ethyl vinyl sulfide enables us, therefore, to conclude that the latter has a higher tendency to undergo free-radical processes than its oxygen analog. This conclusion is confirmed also by a study of the reaction of ethyl vinyl sulfide with hydrogen sulfide. In the presence of traces of oxygen, i.e., under the conditions that have been used previously for this reaction [10], the addition of hydrogen sulfide goes readily and quantitatively, and yields products formed entirely in the direction contrary to Markovnikov's rule:



Ethyl vinyl sulfide polymerizes under the action of sunlight and 2,2'-azobis(2-methylpropionitrile), i.e., again under the conditions favoring free-radical processes. At the same time, its polymerization is not promoted by ionic catalysts, such as SnCl_2 and FeCl_3 , in presence of which ethyl vinyl ether gives a high yield of polymer.

The reaction of ethyl vinyl sulfide with mercuric chloride in water and alcohol is also different from that of its oxygen analog, which combines with mercury salts at the double bond [13]. With mercuric chloride in aqueous or alcoholic solution, the vinyl sulfide loses its ethylthio group, which forms ethylthiomercury chloride:

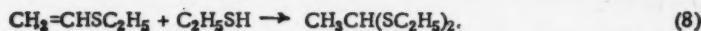


It has been shown previously [2] that this reaction proceeds so quantitatively in ethanol that it can be used for the titrometric determination of vinyl sulfides.

In order to make an approach to an understanding of this interesting reaction, we studied it in a solvent medium that was unable to add at the double bond of the sulfide. For this purpose we selected diethyl ether.

Under these conditions an unstable complex salt (approximate composition $4\text{HgCl}_2 \cdot 3\text{CH}_2=\text{CHSC}_2\text{H}_5$), was isolated; it was rapidly decomposed by alcohol and water with formation of acetaldehyde, hydrogen chloride, and ethylthiomercury chloride. Although this decomposition reaction was far from quantitative, its products nevertheless enable us to suppose that an analogous salt of thionium structure is the first product of the reaction of mercuric chloride with the vinyl sulfide in an ethanol or water medium.

It will be clear from the above that vinyl sulfides differ from their oxygen analogs in showing a much higher tendency to undergo addition in the direction contrary to Markovnikov's rule. On the basis of our experimental results, however, it may be asserted that in certain reactions ethyl vinyl sulfide shows a close analogy to ethyl vinyl ether. Thus, catalytic quantities of sulfur dioxide enable us, as in the case of vinyl ethers [9], to direct the addition of ethanethiol to the vinyl sulfide mainly in accordance with Markovnikov's rule, with formation of 1,1-bis(ethylthio)ethane:



Vinyl sulfides, therefore, like vinyl ethers, can show dual reactivity, reacting by the ionic mechanism in accordance with Markovnikov's rule, and by the free-radical mechanism, in violation of the rule [11]. In no case, therefore, can they be assigned (as is done in a review article by Knunyants and Fokin [14]) to the group of substances of the type of vinyl ketones, alkenyl sulfones, and other substances that always unite with a negative grouping at the end carbon atom of the vinyl group.

EXPERIMENTAL

I. Synthesis of Ethyl Vinyl Sulfide

The synthesis of ethyl vinyl sulfide was carried out, under the conditions described in previous communications [1, 2], by vinylation of the thiol with acetylene in presence of 5% KOH. The results of a series of experiments are given in Table 1.

TABLE 1

Conditions of Synthesis of Ethyl Vinyl Sulfide

Expt. No.	Amt. of thiol taken (g)	Capacity of autoclave (liters)	Amt. of acetylene* (moles per mole of thiol)	Temperature of reaction (°C)	Duration of heating (hr)	Yield of ethyl vinyl sulfide (%)	Yield of 1,2-bis(ethylthio)ethane
1	72.5	2.5	1.3	135-150	2.5	61.3	12.5
2	67.5	2.5	1.34	135-150	2.5	61.0	11.4
3	12.3	0.15	0.5	135-150	1.25	—	82.4
4	14.5	0.15	0.5*3	150-160	1.25*3	56.0	14.8

* In Expts. No. 1-3, one dose of acetylene was given, but in Expt. No. 4 hydroquinone was added and three doses of acetylene were given, each being followed by heating of the autoclave and then cooling.

Expts. No. 1 and 2 were carried out with an excess of acetylene, and the main reaction product was, therefore, ethyl vinyl sulfide. Expt. No. 3 was carried out with a deficiency of acetylene, and, as a result, only 1,2-bis(ethylthio)ethane was isolated (the product of the reaction in accordance with Equation 2 of the ethyl vinyl sulfide formed with the excess of thiol). In Expt. No. 4, 1.3 g of hydroquinone (5 mole-%) was added, and this permitted a number of doses of acetylene to be given (three portions of 0.5 mole each of acetylene per mole of thiol). The addition of hydroquinone retarded the addition of ethanethiol to ethyl vinyl sulfide. However, owing to an appreciable amount of resinification (possibly associated with the high reaction temperature) the yield of vinyl sulfide was no better than that obtained in Expts. No. 1 and 2. By way of example, we shall describe one experiment.

Expt. No. 1. For the vinylation, 72.5 g of ethanethiol, b.p. 34-35°, and 3.6 g of KOH powder were taken. The initial acetylene pressure was 13 atm, i.e., there was 39 g in the autoclave (or 1.3 moles of acetylene per mole of thiol). The reaction mixture was heated at 135-150° for 2 hours 30 minutes, and at the end of the experiment it was washed out into a flask with dry ether (300 ml) and dried over calcined Na_2SO_4 . The ether was driven off from a Favorsky flask, but not completely, owing to the high volatility of ethyl vinyl sulfide. The reaction mixture, together with a small amount of ether, was then fractionated through a 20-plate column, the following fractions being obtained:

Fraction I, b.p. 35-91.5° (750 mm); 5 g; n_D^{20} 1.4680

Fraction II, b.p. 91.5-91.8 (750 mm); 63.3 g; n_D^{20} 1.4760

Resinous residue, 15.4 g

Fraction I, in addition to diethyl ether, contained some moist ethyl vinyl sulfide. Fraction II was ethyl vinyl sulfide, obtained in 61.3% yield. The ethyl vinyl sulfide content of this fraction was determined by titration in accordance with Equation 6, and was found to be 99.4, 99.6%. This method of isolation increased the yield of sulfide boiling over a range of 0.1-0.3° from 40-47% [1] to 61%.

Ethyl vinyl sulfide has a boiling point (corrected to 760 mm) of 91.9-92.2°; $\frac{\Delta t}{\Delta p} = 0.05$ degree/mm (determined from the results of eight distillations at different pressures); d_4^{20} 0.877; n_D^{20} 1.4756; found MR 28.37; calculated MR 28.12.

$\text{C}_4\text{H}_8\text{S}$, Found %: C 54.30; 54.39; H 9.14; 9.05; S 36.25; 36.30
 Calculated %: C 54.49; H 9.14; S 36.37

The literature gives the following constants for ethyl vinyl sulfide: b.p. 90.5-91.5°; d_4^{14} 0.887 [3]; b.p. 91.5-92°; d_4^{15} 0.8691; n_D^{25} 1.4631 [4].

The resinous residue was steam-distilled, extracted with ether, dried, and distilled. A substance (11 g) having the following constants was obtained: b.p. 78° (5 mm); n_D^{20} 1.5114; d_4^{20} 0.9787; found MR 45.97; calculated MR 45.84.

$\text{C}_6\text{H}_{14}\text{S}_2$, Found %: C 48.10; 48.13; H 9.40; 9.43; S 42.17; 42.11
 Calculated %: C 47.95; H 9.39; S 42.66

When oxidized in acetone solution with potassium permanganate, this disulfide gave a disulfone, m.p. 137°. Treatment with an aqueous solution of PdCl_2 gave a complex salt, m.p. 179-180°. When treated with mercuric chloride in alcohol, a yellow coloration was obtained with Methyl orange.

The disulfide isolated has, therefore, the structure of 1,2-bis(ethylthio)ethane, for which the literature gives: b.p. 210-213° at atmospheric pressure, $d_4^{15.5}$ 0.9871 [15]; m.p. of sulfone 137° [16]; m.p. of complex salt with PdCl_2 179-190° [17]. The isomeric diethyl mercaptal $\text{CH}_3\text{CH}(\text{SC}_2\text{H}_5)_2$ gives a sulfone of m.p. 75° [18], and should give an acid reaction with Methyl orange in presence of excess of mercuric chloride [9].

We have obtained also previously undescribed complex salts of 1,2-bis(ethylthio)ethane with one and three molecules of mercuric chloride. 1,2-Bis(ethylthio)ethane (0.47 g) was mixed with 4.5 ml of a 20% alcoholic solution of mercuric chloride. The resulting precipitate, after recrystallization from alcohol and vacuum drying, melting at 99.5-100°.

$\text{C}_6\text{H}_{14}\text{S}_2\text{HgCl}_2$, Found %: Cl 17.18; 17.14; S 15.27; 15.32
 Calculated %: Cl 16.81; S 15.20

The salt obtained as above (2 g) was shaken mechanically for 60 hours with an alcoholic solution of mercuric chloride (1.5 g of HgCl_2 in 10 ml of ethanol). The precipitate, after recrystallization from alcohol and vacuum drying, was obtained in the form of needles, m.p. 162°.

Found %: C 7.35; 7.44; H 1.58; 1.58; S 6.82; 6.71; Cl 22.3; 22.1
 $C_6H_{14}S_2 \cdot 3HgCl_2$. Calculated %: C 7.46; H 1.46; S 6.64; Cl 22.03

II. Reaction of Ethyl Vinyl Sulfide with Ethanethiol

All experiments were carried out with an excess of about one molecular proportion of ethanethiol, and both the thiol and the ethyl vinyl sulfide were freshly distilled for use.

a) Addition of C_2H_5SH to $C_2H_5SCH=CH_2$ in presence of air. To 3.6 g of ethyl vinyl sulfide, contained in a flask fitted with a stirrer and cooled with ice water, 4.2 g of ethanethiol was added, and the mixture was set aside overnight. The excess of thiol was distilled off, and 5.3 g (88.3%) of 1,2-bis(ethylthio)ethane then came over at 94-95° (7 mm); it had n_D^{20} 1.5110. The product did not give an acid reaction with Methyl orange after addition of excess of mercuric chloride. The addition of ethanethiol to ethyl vinyl sulfide was entirely in the direction contrary to Markovnikov's rule.

b) Addition of C_2H_5SH to $CH_2=CHSC_2H_5$ in a vacuum in presence of traces of oxygen. The experiment was carried out in the three-ampoule apparatus described in a previous communication [9]. Ethyl vinyl sulfide (6 g) was introduced into an ampoule having a side tube, and ethanethiol (8.6 g) was introduced into another, similar ampoule. These substances were then vacuum-distilled into the third ampoule, which had a capillary neck and was cooled with liquid nitrogen. The whole system was evacuated, and the ampoule was sealed off. It was then heated at 60-70° for 25 hours, with some interruptions. Fractionation yielded 3.5 g of the thiol (in the trap) and 9.3 g (93%) of 1,2-bis(ethylthio)ethane, b.p. 61° (2.8 mm), n_D^{20} 1.5112. In presence of traces of oxygen, the addition of ethanethiol to ethyl vinyl sulfide was again in the direction contrary to Markovnikov's rule.

c) Addition of C_2H_5SH to $CH_2=CHSC_2H_5$ in presence of hydroquinone. The experiment was carried out as described above, with the exception that 0.75 g (5 mole-%) of hydroquinone was introduced into the ampoule having the capillary neck. The ethyl vinyl sulfide (6 g) and ethanethiol (8 g) were distilled before the experiment in a current of dry nitrogen. After the ampoule had been heated at 60-70° for 25 hours with some interruptions, the reaction mixture was fractionated. At room temperature and at a residual pressure of 6 mm, 10 g of substance came over directly from the ampoule and was collected in a trap; fractionation of this under atmospheric pressure yielded 5.5 g of unchanged thiol and 2.5 g of ethyl vinyl sulfide. The residue was washed from the ampoule with ether, and the ether extract was washed with alkali to remove hydroquinone, dried over calcined Na_2SO_4 , and distilled, when 2.2 g of a substance of b.p. 72-80° (10 mm) and n_D^{20} 1.5056 was obtained. After redistillation the constants of the product were b.p. 72-74° (10 mm); n_D^{20} 1.5025; d_4^{20} 0.9706; found MR 45.74; calculated MR 45.84.

All of these constants, and also the formation of a sulfone of m.p. 75° by permanganate oxidation, indicate that this substance was the diethyl mercaptal $CH_3-CH(SC_2H_5)_2$. Values found for the mercaptal content were 99.8%, 100.7%, determined by titration after addition of excess of mercuric chloride in ethanol, when reaction occurs according to the equation:



The yield of the mercaptal was 36.6%. The somewhat high refractive index and the extended boiling range during the first fractionation indicate the possible presence of 1,2-bis(ethylthio)ethane as impurity. The presence of hydroquinone retarded the reaction of addition contrary to Markovnikov's rule and made it possible for reaction in accordance with this rule to occur.

d) Addition of C_2H_5SH to $CH_2=CHSC_2H_5$ in presence of SO_2 . The thiol (4.0 g) was cooled in an ampoule with a mixture of dry ice and acetone, 0.2 g of SO_2 was condensed in the ampoule, and then 5.3 g of cooled ethyl vinyl sulfide was added. The ampoule was transferred to a Dewar vessel containing liquid nitrogen, evacuated, and sealed off. After four days the ampoule was opened, and the mixture was fractionated, yielding:

Fraction I, b.p. 66-70° (10 mm); 5.5 g; n_D^{20} 1.5055

Fraction II, b.p. 70-80° (10 mm); 2.0 g; n_D^{20} 1.5100

Resinous residue, 1 g

After refractionation, Fraction I was titrated for mercaptal and gave values of 91.4%, 91.9%; the yield of this product was 51%. Fraction II corresponded in its boiling point and refractive index to the isomeric 1,2-bis(ethylthio)ethane. In the presence of SO_2 addition occurred mainly in accordance with Markovnikov's rule.

III. Reaction of H_2S with $CH_2=CHSC_2H_5$

Ethyl vinyl sulfide (8.9 g) was introduced into an ampoule, into which 5.6 g (1.5 moles per mole of ethyl vinyl sulfide) of hydrogen sulfide was then condensed. The cooled ampoule was evacuated and sealed off. After

2.5 months the ampoule was opened, the excess of hydrogen sulfide was evaporated off, and the mixture was fractionated, yielding:

Fraction I, b.p. 60° (9 mm); 7.1 g

Fraction II, b.p. 161° (9 mm); 4.2 g

Fraction I was 2-ethylthioethanethiol $C_2H_5SCH_2CH_2SH$, obtained in 58.6% yield.

After refractionation this substance had b.p. 60° (9 mm); n_D^{20} 1.5273; d_4^{20} 1.0337; found MR 36.47; calculated MR 36.53.

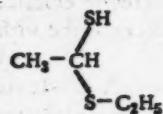
Found %: C 39.67; 39.62; H 8.33; 8.36; S 52.05; 52.09

$C_8H_{18}S_2$.

Calculated %: C 39.30; H 8.24; S 52.46

For this substance the literature [19] gives b.p. 188° at atmospheric pressure.

This thiol was stable and was not decomposed by strong hydrochloric acid; the isomeric 1-ethylthioethanethiol



should be decomposed by acid with formation of "trithioacetaldehyde" (2,4,6-trimethyl-s-trithiane), like the previously described 1-alkoxyethanethiols [20].

Fraction II gave no acid reaction with Methyl orange when mixed with excess of mercuric chloride. It was bis(2-ethylthioethyl) sulfide obtained in 40.3% yield. At room temperature it solidified to a crystalline mass. It had n_D^{20} 1.5460; d_4^{20} 1.0542; found MR 63.21; calculated MR 63.04.

Found %: C 45.97; 45.92; H 8.74; 8.66; S 45.74; 45.35

$C_8H_{18}S_3$.

Calculated %: C 45.66; H 8.62; S 45.72

According to the literature [20], this trisulfide has b.p. 173-175° (21 mm) and m.p. 17°.

In presence of traces of oxygen, hydrogen sulfide adds to ethyl vinyl sulfide entirely in the direction contrary to Markovnikov's rule.

IV. Polymerization of Ethyl Vinyl Sulfide

a) Polymerization of ethyl vinyl sulfide in presence of $FeCl_3$ and $SnCl_2$. The results of this series of experiments are given in Table 2.

TABLE 2

Polymerization of Ethyl Vinyl Sulfide in Presence of $FeCl_3$ and $SnCl_2$. Amount of ethyl vinyl sulfide taken: 2.65 g, i.e., 3 ml

Expt. No.	Catalyst as alcoholic solution (drops)		Yield of resinous residue (g)	Amount of unchanged monomer (g)
	1% $SnCl_2$	5% $FeCl_3$		
1	2	-	0.1	2.3
2	4	-	0.1	2.3
3	-	1	0.1	2.4
4	-	2	0.1	2.2
5	-	3	0.3	2.2
6	-	-	0.1	2.3

The polymerization was carried out in sealed tubes heated, with some interruptions, for 54 hours at 50°. It will be clear from the results in Table 2, that under these conditions, $SnCl_2$ and $FeCl_3$ do not promote the polymerization of ethyl vinyl sulfide. Addition of catalyst to the boiling substance does not increase the yield of polymer, whereas, under these conditions, ethyl vinyl ether gives high yields of highly viscous polymers [11, 12].

b) Polymerization of ethyl vinyl sulfide in presence of sunlight. A sealed glass tube containing 2.5 g of ethyl vinyl sulfide was exposed to sunlight. By the tenth day the liquid had acquired the consistency of glycerol. After 2.5 months, fractionation in a current of dry nitrogen yielded 0.8 g of monomer (n_D^{20} 1.4768). The polymer was freed from monomer in a vacuum

desiccator, at first at room temperature, and then at 40-45°. The yield of polymer was 1.5 g (60%). The polymer was found to be soluble in the cold in dioxane, dichlorethane, and ether, but insoluble in ethanol. It was not found possible to determine the molecular weight by the cryoscopic method owing to the very small depression; the molecular weight was, therefore, higher than 5000.

Found %: C 54.58; 54.53; H 9.21; 9.17; S 36.09; 36.33
 $(C_4H_8S)_p$ Calculated %: C 54.49; H 9.14; S 36.37

c) Polymerization of ethyl vinyl sulfide in presence of 2,2'-azobis(2-methylpropionitrile). A mixture of 5 g of ethyl vinyl sulfide and 0.01 g (0.2% by weight) of 2,2'-azobis(2-methylpropionitrile) was heated continuously for 80 hours in a sealed tube in a thermostat at 60°. The contents of the tube were then dissolved in 10 ml of dry benzene, and the solution was poured slowly into 200 ml of dry methanol. The reprecipitation was repeated twice, and the yield of polymer was then 2.5 g (50% on the amount of ethyl vinyl sulfide taken). The amount of unchanged monomer, determined in the methanol solutions from the reprecipitations (addition of excess of mercuric chloride and titration with 0.1 N NaOH) was 2.45. The polymer was dried at 60° in a vacuum to constant weight.

Found %: C 54.86; 55.01; H 9.14; 9.03; S 36.27; 36.27
 $(C_4H_8S)_p$ Calculated %: C 54.49; H 9.14; S 36.37

V. Reaction of Ethyl Vinyl Sulfide with Mercuric Chloride

a) Reaction of ethyl vinyl sulfide with an alcoholic solution of mercuric chloride. Ethyl vinyl sulfide (0.13 g) was treated with 4.5 ml of a 20% solution of mercuric chloride in ethanol, and the mixture was set aside overnight. The precipitate was filtered off, washed with alcohol and with ether, and vacuum-dried to constant weight. The yield of precipitate was 0.37 g (96.2%). The ethylthiomercury chloride was recrystallized from boiling xylene, washed with alcohol and with ether, and vacuum-dried. It did not melt when heated to 200°, but it slowly decomposed at about 300-350°, which is in accord with the literature [21].

Found %: S 10.78; 10.73
 $C_2H_5SHgCl_2$ Calculated %: S 10.79

It has been shown above that, when the sulfide is treated with a 20% solution of mercuric chloride in ethanol, the formation of hydrogen chloride is also quantitative in accordance with Equation 6; subsequent titration with 0.1 N NaOH provides a method for the quantitative analysis of the sulfide.

b) Reaction of ethyl vinyl sulfide with an aqueous solution of mercuric chloride. Ethyl vinyl sulfide (1.1 g) was introduced into 75 ml of an aqueous solution of mercuric chloride (4.1 g of $HgCl_2$ in 75 ml of water). On the next day the reaction mixture was transferred to a flask and fractionated in a continuous current of dry nitrogen. The aqueous part was collected in receivers, and the vapor was passed on through a trap containing alcohol and cooled with snow and salt. The contents of the trap had a strong odor of acetaldehyde and gave a magenta color with Schiff's reagent; the aqueous distillate was acid to Methyl orange. The precipitate weighed 3.13 g (87% yield). It was treated as in the previous experiment, and it did not melt below 200°, i.e., it had the properties of ethylthiomercury chloride.

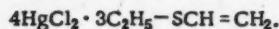
TABLE 3
 Decomposition of the Complex with Water and with Alcohol

Expt. No.	Amount of sulfide (g)	Amount of $HgCl_2$ (g) in 50 ml ether	Yield of pink complex salt (g)	Ppt. treated with	Yield of ethylthiomercury chloride (%)
1	1.15	4	5.4	H_2O	23
2	1.05	4	5.2	C_2H_5OH	21

c) Reaction of ethyl vinyl sulfide with an ethereal solution of mercuric chloride. Ethyl vinyl sulfide (70.1 g) was mixed with 25 ml of an ethereal solution of mercuric chloride (1 g of mercuric chloride in 25 ml of absolute ether). After a time a pink precipitate formed, and, when the ether was removed, this began to change rapidly in color, through lilac to black. The precipitate melted at 32-34°, sintering into a black lump.

Found %: C 10.15; 10.21; H 1.97; 1.84; S 8.05; 7.86
 $C_{12}H_{24}S_3 \cdot 4HgCl_2$. Calculated %: C 10.55; H 1.76; S 7.04

This composition corresponds approximately to the formula



This complex salt of ethyl vinyl sulfide with mercuric chloride was unstable, and it decomposed readily when treated with alcohol or water. The aqueous or alcoholic solution then acquired an aldehyde reaction and acidity, and the pink complex salt was converted into a white infusible precipitate of ethylthiomercury chloride (Table 3); this conversion was not, however, quantitative.

SUMMARY

1. Conditions have been found for the synthesis of ethyl vinyl sulfide in 60% yield.
2. It has been shown that ethanethiol and hydrogen sulfide add to ethyl vinyl sulfide, in the air and in presence of traces of oxygen, in the direction contrary to that required by Markovnikov's rule; but, in presence of hydroquinone or of the acid catalyst SO_3 , addition of the thiol proceeds in accordance with the rule.
3. It has been shown that polymerization of ethyl vinyl sulfide does not occur in presence of the ionic catalysts FeCl_3 and SnCl_3 , but occurs in presence of 2,2'-azobis(2-methylpropionitrile), under the action of sunlight, and when kept for a long time.
4. The reaction of ethyl vinyl sulfide with mercuric chloride in alcoholic and aqueous solutions leads to the formation of a mercurated salt of ethanethiol, but in ethereal solution the product is an unstable complex salt, which is decomposed by water and alcohol.
5. It has been shown that ethyl vinyl sulfide, although the sulfur analog of ethyl vinyl ether, has a considerably greater tendency to undergo addition reactions that are contrary to Markovnikov's rule and have a free-radical character.

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* See Consultants Bureau Translation, page 439 (this issue).

** See Consultants Bureau Translation, page 325.

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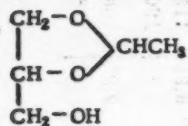
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REACTIONS BETWEEN VINYL COMPOUNDS AND MULTIFUNCTIONAL COMPOUNDS

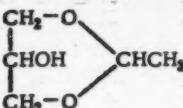
COMMUNICATION 2. REACTIONS OF VINYL ETHERS WITH POLYVINYL ALCOHOL

M. F. Shostakovsky, V. V. Zhebrovsky, and M. A. Medelyanovskaya

In our communication [1] relating to the reactions of alkyl vinyl ethers (ethyl vinyl and butyl vinyl) with glycerol, it is shown that the mobile hydrogens of the free hydroxyl eliminate alkoxy groups from the partial mixed acetals with formation of cyclic acetals of glycerol. As a result of these transformations, the following acetals were obtained:

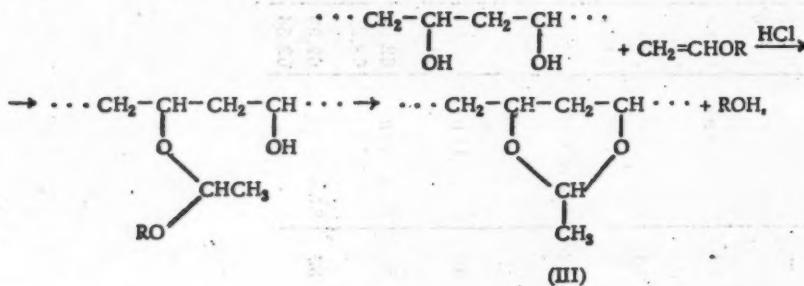


(I)



(II)

In connection with the discovery of this method of synthesizing cyclic acetals, it was considered to be of interest to study the reaction of vinyl ethers with polyhydric alcohols, such as polyvinyl or polyallyl alcohols, which have much higher numbers of hydroxyl groups in their molecules than glycol or glycerol. In this case the reaction may be represented as follows:



(R is alkyl or aryl).

In the literature there is only an indication of the possibility of the reaction of polyvinyl alcohol with the lower alkyl vinyl ethers [2].

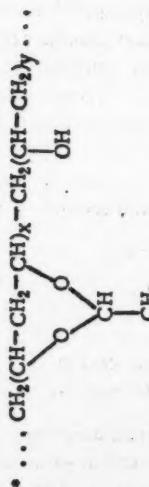
Our investigations have established that, when alkyl and aryl vinyl ethers react with polyvinyl alcohol, a polyacetal of polyvinyl alcohol (III) and the corresponding monohydric alcohol are formed, i.e., the reaction proceeds analogously to the synthesis of acetals from glycerol. The formation of polyacetals of polyvinyl alcohol by reaction of the latter with vinyl ethers evidently also passes through a mixed partial acetal, which, being unstable, reacts with formation of cyclic polyacetals and separation of a monohydric alcohol. When there is excess of vinyl ether, the alcohol or phenol that separates reacts with this excess and forms the corresponding acetal. These ideas are confirmed, first by the fact that in the course of the syntheses of polyacetals no appreciable amounts of acetaldehyde were detected, and second by the high yields of acetals.

In the investigation of the reaction between polyvinyl alcohol and vinyl ethers, the examples of the latter selected were butyl vinyl and phenyl vinyl ethers, and the ratio of components was varied and various catalysts were taken in various amounts, with the object of ensuring that the conditions were such as to exclude the possibility of the hydrolysis of the vinyl ether. Analysis of the resulting polyacetals of polyvinyl alcohol showed that the replacement of hydroxyl groups of the polyalcohol proceeded almost to completion under various conditions, attaining 95-97% of the theoretical value.

The observed discrepancies between the determined and calculated values in the elementary composition of the polyacetals, which were somewhat higher than those normally accepted for pure individual compounds, must be explained on the basis of the nature of highly polymeric substances.

Analysis of Polyacetals Obtained by the Reaction of Vinyl Ethers with Polyvinyl Alcohol

Components, and their amounts (basal moles)	Experimental conditions			Elementary composition			Chemical composition			Rel. vis coast of 1% soln. in dichloro- ethane	Yield of poly- acetal (% of theo- retical)	
	Butyl vinyl ether (moles)	Phenyl vinyl ether (moles)	Amount of catalyst (g)	Temp. (°C)	Time	found %C	calculated %C	%H	Hydroxyl No.	OH groups (%)		
+	-	-	-	-	-	53.29	54.54	9.09	1064.0	32.3	-	-
1	0.5	-	0.146 HCl	50	5 mins	53.15 61.07	53.15 62.32*	9.02 8.74	113.58 116.40	3.40 3.54	43.77 44.42	3.67 44.42
1	1	-	0.292 HCl	50	8 mins	61.83 61.65	61.83 61.65	8.73 8.97	62.29 62.29	8.80 8.80	120.0 120.0	3.70 44.41
1	0.5	-	0.042 HCl	18-20	48 hrs	60.92 61.10	60.92 61.10	8.88 9.11	62.42 62.42	8.79 8.79	95.10 99.80	43.39 43.12
1	1	-	0.131 H ₃ PO ₄	50	10 mins	61.07 61.33	61.07 61.33	9.31 9.14	61.83 61.83	8.82 8.82	188.0 188.0	5.73 43.35
1	-	0.5	0.218 HCl	50	2 hrs 40 mins	62.35 62.20	62.35 62.20	9.01 9.09	62.29 62.29	8.80 8.80	115.90 120.40	3.54 3.65
1	-	1	0.146 HCl	50	2 hrs 50 mins	62.34 62.34	62.34 62.34	9.00 8.99	61.80 61.80	8.82 8.82	196.20 185.30	5.95 5.64



EXPERIMENTAL

The sample of polyvinyl alcohol used in this work had the following characteristics: content of acetate groups 1.82%; acid number 1.1; content of volatile substances, determined by drying to constant weight over calcium chloride, 3.31%; specific viscosity of a 1% aqueous solution, determined in an Ostwald viscometer, 1.93. The polyvinyl alcohol was brought to a highly dispersed condition by grinding in a ball mill and passage through a sieve having 10,000 mesh per sq.cm.

The vinyl ethers had the following constants: butyl vinyl ether, b.p. 93-94°, n_D^{20} 1.4030; phenyl vinyl ether, b.p. 46-47° (11-12 mm); n_D^{20} 1.5228.

Procedure

The synthesis was carried out in a three-necked flask fitted with stirrer, mercury seal, thermometer, and reflux condenser attached to a spiral receiver cooled to -40 to -60°. The polyvinyl alcohol and vinyl ether were suspended in chloroform. After 30 minutes the catalyst (hydrochloric acid) was added, and the reaction was carried out at room temperature or at 50°. When reaction was complete, as indicated by the formation of a homogeneous clear solution, the reaction mixture was neutralized with ammonia. The reaction product was precipitated with ether, and was then washed with 150 ml of distilled water and air-dried.

When butyl vinyl ether was used, before precipitation of the product with ether the bulk of the volatile part was distilled off under reduced pressure and collected in the receivers and two spiral traps cooled to -40 to -60°. The dried product was purified by two reprecipitations from acetone solution by means of distilled water, and it was then dried to constant weight over calcium chloride and subjected to analysis. Half of the diethyl ether from the precipitation was distilled, to separate volatile reaction products, and the other half was transferred to a weighed porcelain dish and evaporated in the air. The wash water, and also the aqueous acetone solutions from the reprecipitation of the polyvinyl acetals were also evaporated in the air. The products so isolated were taken into account in the general balance sheet of the reaction.

Analysis of the purified and dried polyvinyl acetal was carried out as follows: determination of acetal groups was carried out by the method developed by Soloveichik and Balandina [3] for the analysis of polyvinylbutyral. The hydroxyl numbers were determined by the acetic acid-pyridine method of Barley and Belsing [4]. The results of the analyses of polyvinyl acetals are given in the table.

Reaction of Butyl Vinyl Ether with Polyvinyl Alcohol

a) 0.5 Mole of butyl vinyl ether per basal mole of polyvinyl alcohol. Polyvinyl alcohol (4.4 g, i.e., 0.1 basal mole) and butyl vinyl ether (5.0 g, i.e., 0.05 mole) were suspended in 30 ml of chloroform. After 30 minutes, ten drops (0.146 g) of hydrochloric acid were added, the mixture was heated to 50°, and reaction was complete in five minutes. The yield of purified polyacetal was 5.3 g (93%). From the ether solution, 1.08 g (29.2%) of butyl alcohol was isolated (this contained chloroform impurity that was difficult to remove). The boiling point of the butyl alcohol was 113-114°, and the value of n_D^{20} was 1.4032; it reacted vigorously with sodium and gave the characteristic color for alcohols in Agulhon's reaction [5], but it also gave a positive Beilstein test for chlorine.

b) One mole of butyl vinyl ether per basal mole of polyvinyl alcohol. Polyvinyl alcohol (4.4 g, i.e., 0.1 basal mole) and butyl vinyl ether (10 g, i.e., 0.1 mole) were suspended in 30 ml of chloroform. After 30 minutes, 20 drops (0.292 g HCl) of hydrochloric acid were added, and five minutes later the temperature of the reaction mixture had risen from 50° to 58°. Reaction was complete eight minutes after the addition of catalyst. After the purification treatment, 5.23 g (92%) of the polyacetal was obtained. Distillation of the ether solution yielded:

Fraction I, b.p. 38-41° (15 mm); 2.15 g; n_D^{20} 1.4045

Fraction II, b.p. 74-78° (15 mm); 2.71 g; n_D^{20} 1.4115

Redistillation of Fraction I yielded a substance of b.p. 113-114°, n_D^{20} 1.4028, having the characteristic odor of butyl alcohol and reacting vigorously with sodium.

Two redistillations of Fraction II yielded a substance having b.p. 77-80° (15 mm), d_4^{20} 0.8319 and n_D^{20} 1.4118. Its constants differed somewhat from those given in the literature for the dibutyl acetal: b.p. 184-185°; d_4^{20} 0.8267; n_D^{20} 1.4090 [6]; this, as already indicated above, is explained by the presence of chloroform impurity, which we did not succeed in separating.

Found %: C 68.50; 68.40; H 12.57; 12.60

$C_{18}H_{22}O_2$. Calculated %: C 68.97; H 12.65

c) Experiment in presence of traces of catalyst (hydrochloric acid). The experiments described, in which 0.5 mole or one mole of butyl vinyl ether reacted with one basal mole of polyvinyl alcohol, were performed in presence of a comparatively large amount of aqueous hydrochloric acid and at an elevated temperature, and these conditions could themselves lead to hydrolysis of the vinyl ether. At the same time, therefore, experiments were carried out with a very small amount of hydrochloric acid. The quantities of the original components were kept the same, but the experiments were carried out in presence of three drops of hydrochloric acid (0.042 g) and at room temperature. Under these conditions, and with 0.5 mole of butyl vinyl ether per basal mole of polyvinyl alcohol, reaction was complete in 48 hours. After treatment of the resulting solution according to the procedure described above, 5.23 g (91%) of purified polyacetal and 0.89 g (24%) of butyl alcohol (b.p. 113-114°, n_D^{20} 1,3982) were obtained.

d) Experiment in presence of phosphoric acid (as catalyst). In order to exclude the effect of water on the reaction between polyvinyl alcohol and vinyl ethers, an experiment was carried out in presence of anhydrous phosphoric acid (five drops, 0.1315 g) at 50°. Reaction was complete in ten minutes with rise in the temperature of the mixture to 61.5°. The amounts taken for reaction were 4.4 g of polyvinyl alcohol and 10 g (0.1 mole) of butyl vinyl ether, and the products isolated were 4.95 g (86.2%) of purified polyacetal and 5.65 g (65%) of acetaldehyde dibutyl acetal, b.p. 77-80° (15 mm); n_D^{20} 1.4096; n_D^{20} 1.4120.

Analysis of Acetaldehyde Dibutyl Acetal

Found %: C 68.33; 68.28; H 12.66; 12.57

$C_{16}H_{22}O_2$. Calculated %: C 68.97; H 12.65

Reaction of Phenyl Vinyl Ether with Polyvinyl Alcohol

a) 0.5 Mole of phenyl vinyl ether per basal mole of polyvinyl alcohol. Polyvinyl alcohol (6.6 g) and phenyl vinyl ether (9.0 g, i.e., 0.075 mole) were suspended in 45 ml of chloroform. After thirty minutes, 15 drops of hydrochloric acid (0.218 g) were added and the mixture was heated to 50°, and after a further 2 hours 40 minutes, reaction was complete, the temperature having risen to 58°. The yield of purified polyacetal was 8.34 g (98.7%).

The ether solution was divided into two parts, transferred to two porcelain dishes, and exposed to air for evaporation of solvent. In the first dish, after the evaporation there remained 3.45 g (49.3% of the calculated amount) of colored syrupy material, having n_D^{20} 1.5412 and giving a characteristic color for phenol with ferric chloride. The residue in the second dish was used for the steam distillation of phenol. For the quantitative determination of the phenol isolated, Koppeschaar's method was used [7], the amount found being 1.752 g.

b). One mole of phenyl vinyl ether per basal mole of polyvinyl alcohol. A mixture of 4.4 g (0.1 basal mole) of polyvinyl alcohol and 12.0 g (0.1 mole) of phenyl vinyl ether was suspended in 30 ml of chloroform. After 30 minutes, ten drops of hydrochloric acid (0.146 g) were added and the mixture was heated to 50°. Reaction was complete in 2 hours 50 minutes. The yield of purified polyacetal was 5.17 g (90.7%).

After removal of ether by evaporation, the residue was 8.65 g of a colored syrupy material having n_D^{20} 1.5522. After repeated vacuum distillation this yielded 1.98 g (18.5% of the calculated amount) of a substance, b.p. 169° (28 mm) and n_D^{20} 1.5565, corresponding to acetaldehyde diphenyl acetal, and also 0.21 g of crystalline phenol.

Analysis of Acetaldehyde Diphenyl Acetal

Found %: C 77.97; 78.02; H 6.79; 6.81

$C_{14}H_{14}O_2$. Calculated %: C 78.51; H 6.54

SUMMARY

1. A study has been made of the reactions between polyvinyl alcohol and butyl vinyl and phenyl vinyl ethers, the proportions of components being varied.

2. It has been shown that reaction between polyvinyl alcohol and butyl vinyl or phenyl vinyl ether leads to the formation of polyacetals of polyvinyl alcohol.

3. It is possible that the formation of the polyacetals of polyvinyl alcohol passes through the stage of mixed acetals, which subsequently undergo cyclization.

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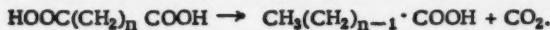
MACROMOLECULAR COMPOUNDS

COMMUNICATION 61. DECARBOXYLATION OF DICARBOXYLIC ACIDS DURING POLYCONDENSATION

V. V. Korshak and S. V. Rogozhin

The decomposition of adipic acid with evolution of carbon dioxide in the course of the polycondensation of the acid with 1,6-hexanediamine was first discovered by one of us in collaboration with Zamyatina [1]. It was shown that the decomposition of the acid was of great significance in the polycondensation reaction, and this induced us to make a more detailed study of this reaction for various dicarboxylic acids under polycondensation conditions.

In a systematic study of the decarboxylation of dicarboxylic acids by heat, we examined oxalic, malonic, succinic, glutaric, adipic, pimelic, azelaic, and sebatic acids [2, 3]. It was found that the thermal decomposition of dicarboxylic acids resulted in the formation of carbon dioxide, monocarboxylic acids, sometimes cyclic ketones, and other products. The formation of a monocarboxylic acid may be represented by the following equation:



With increase in the length of the carbon chain of the acid its stability to the action of high temperature increases and its decarboxylation temperature rises correspondingly from 140° for malonic acid to 350° for sebatic acid. It was noted that acids having an even number of carbon atoms decompose at a higher temperature than acids having an odd number of carbon atoms (the number of carbons in the chain being greater than one). The results obtained pointed to the conclusion that, in the polycondensation of dicarboxylic acids, the temperature conditions must be such as to obviate decomposition of the acid. The conversion of dicarboxylic acids into monocarboxylic acids or cyclic ketones as a result of decarboxylation affects the proportions of starting substances, which results in reduction in the molecular weight of the polymers formed, as was shown by one of us with Rafikov [4], with Golubev [5], with Kolesnikov [6], and with others, the cause of this being the premature termination of the chain [7, 8].

The object of the present investigation was to determine the effect on the decomposition of dicarboxylic acids of exposure to the conditions of polycondensation with other bifunctional compounds. The presence of a second compound, and also reaction with this formation of macromolecular compounds, is bound to have an effect on the behavior of the dicarboxylic acids. It was of great interest also to study the effect of the decarboxylation of the acids on the process of macromolecule formation. In order to obtain an answer to these questions we have studied the decomposition of oxalic, malonic, succinic, adipic, and sebatic acids under the conditions of their polycondensation with ethylene glycol.

EXPERIMENTAL

The rate of the decomposition of the dicarboxylic acid was determined from the amount of the resulting carbon dioxide, which was absorbed either in standard alkali or in U-tubes filled with soda asbestos, the amount evolved then being determined by the increase in weight. The polycondensation reaction was carried out in a current of dry nitrogen, which was first purified from oxygen and carbon dioxide. A diagram of the apparatus is given in Fig. 1.

Equimolecular amounts of the acid and ethylene glycol were placed in a test tube and heated in a bath containing Wood's metal. Nitrogen, dry and purified from oxygen and carbon dioxide, was passed continuously into the tube. In the polycondensation of ethylene glycol with succinic, adipic, and sebatic acids, the duration of the reaction was in each case nine hours. During the first two hours, the nitrogen was passed through the reflux condenser 2 and the distillation condenser 3, and carried away the carbon dioxide and other volatile products. The presence of the reflux condenser enables loss, due to volatility, of the original substances to be avoided.

After two hours, when the original compounds had entered almost entirely into the reaction, the nitrogen, containing water vapor and carbon dioxide, passed only through the condenser 3, in which most of the water vapor condensed. The remaining traces of water vapor were absorbed in the Drechsel 5, containing concentrated sulfuric acid and in a U-tube containing calcined calcium chloride. After being freed from water vapor, the nitrogen and the carbon dioxide formed by the breakdown of carboxyl groups passed to the absorption system, in which the carbon dioxide was absorbed.

Experimental Results

The experiments on the polycondensation of ethylene glycol with oxalic and malonic acids were carried out at 90° and 140°. The carbon dioxide evolved was absorbed with a solution of caustic soda. The results for oxalic acid are given in Table 1, and those for malonic acid in Table 2. In these experiments no polyesters were formed, and the reaction products were, therefore, not investigated in greater detail.

TABLE 1

Decomposition of Oxalic Acid when Heated with Ethylene Glycol

No.	Duration of heating (hr)	Amount of acid decomposed (%) at					
		90°	100°	110°	120°	130°	140°
1	0.5	0.22	0.73	1.90	2.92	5.70	21.90
2	1.0	0.76	1.54	4.90	6.00	14.10	34.50
3	2.0	1.38	3.28	10.40	15.30	29.30	45.60
4	3.0	1.97	4.75	14.50	24.10	42.70	48.60
5	4.0	2.62	6.90	20.50	31.40	49.30	49.80
6	5.0	3.38	9.01	24.30	35.70	49.60	49.90
7	6.0	4.23	11.00	—	40.10	50.00	50.00

TABLE 2

Decomposition of Malonic Acid when Heated with Ethylene Glycol

No.	Duration of heating (hr)	Amount of acid decomposed (%) at				
		90°	100°	110°	120°	140°
1	0.5	1.50	3.10	5.95	16.50	27.30
2	1.0	4.20	6.40	11.90	24.40	33.60
3	2.0	6.70	13.40	20.60	30.30	37.90
4	3.0	9.40	19.30	25.80	36.40	41.40
5	3.0	12.30	22.40	28.50	38.10	43.20
6	5.0	15.60	25.50	31.60	38.10	44.90

In the case of succinic, adipic, and sebatic acids, polycondensation occurred when they were heated with ethylene glycol with formation of polyesters. The nature and number of the end groups of the polyester, and also its molecular weight, were determined for each sample for the various reaction temperatures, and they are given in tables: the results for succinic acid in Table 3, for adipic acid in Table 4, and for sebatic acid in Table 5.

TABLE 3

Polycondensation of Succinic Acid with Ethylene Glycol

Reac- tion temp (°C)	Amt. of COOH groups split off (%)	Characteristics of polyester						
		ml of 0.1 N alkali con- sumed per g of polyester in determining		Amt. of COOH groups split off, calcd. from titration data	sp. viscosity of 0.5% solution	molecular weight		
		OH groups	COOH groups			by hydroxyl groups	by carboxyl groups	by viscosity
240	2.81	10.60	10.65	0.51	0.026	945	949	840
250	7.01	8.00	8.25	2.30	0.037	1250	1215	1190
260	14.25	6.25	4.78	20.30	0.053	1600	2095	1680
270	21.30	7.34	4.01	35.30	0.051	1360	2490	1610
280	—	13.67	3.40	68.24	0.030	734	2945	940

In the second column of Table 3 we give the amount of carboxyl groups split off as a percentage of the total amount; these figures are calculated from the amount of carbon dioxide evolved. The figures in the fifth column of Table 3 (amount of carboxyl groups eliminated from the polyester) were calculated on the basis of the results of the titration of the carboxyl end groups of the polyester, and they indicate the deficiency in the amount of carboxyl groups in comparison with the amount to be expected on the basis of the viscometric determination of molecular weight.

TABLE 4

Polycondensation of Adipic Acid with Ethylene Glycol

Reaction temp. (°C)	Amt. of COOH groups split off (%)	Characteristics of polyester						
		ml of 0.1 N alkali con- sumed per g of polyester in determining		Amt. of COOH groups split off, calcd. from titration data	sp. viscosity of 0.5% solution	molecular weight		
		OH groups	COOH groups			by hydroxyl groups	by carboxyl groups	by viscosity
180	0.33	—	31.20	—	0.014	—	320	426
190	0.53	—	31.55	—	0.015	—	317	474
200	0.74	—	22.25	—	0.017	—	448	525
210	1.17	—	13.90	0.10	0.024	—	721	720
220	2.12	12.15	10.00	5.5	0.031	800	1000	945
230	4.75	10.00	7.55	4.20	0.042	1000	1828	1270
240	9.54	4.96	6.24	—	0.056	2020	1600	1670
250	14.65	4.74	4.28	—	0.088	2100	2350	2670
260	—	4.02	3.92	17.10	0.071	2500	2548	2140
270	20.80	6.90	2.95	40.90	0.066	1450	3390	2000
280	29.00	7.70	2.32	65.80	0.049	1300	4300	1470

TABLE 5

Polycondensation of Sebacic Acid with Ethylene Glycol

Reaction temp. (°C)	Amt. of COOH groups split off (%)	Characteristics of polyester					
		ml of 0.1 N alkali con- sumed per g of polyester in titration of COOH groups	Amt. of COOH groups split off, calcd. from titration data	sp. viscosity of 0.5% solution	molecular weight		
					by carboxyl groups	by viscosity	
230	0.002	9.12	—	0.030	1000	1100	
240	0.003	6.48	2.60	0.042	1540	1500	
250	0.005	5.20	4.62	0.057	1950	1860	
260	0.004	4.36	7.40	0.059	2300	2130	
270	0.012	3.68	5.10	0.072	2740	2600	
280	0.023	3.22	4.50	0.082	3100	2960	

The amount of carboxyl groups eliminated from the polyester characterizes the extent to which the high temperature has affected its carboxyl end groups. A knowledge of this quantity permits us to estimate the difference in thermal stability of the carboxyl groups in the original acid, and of those in the polyester.

Discussion of Results

The investigation of the decomposition of dicarboxylic acids when heated in presence of glycols, i.e., under polycondensation conditions, shows that in the free condition dicarboxylic acids decompose considerably more slowly than under polycondensation conditions. For example, we have previously established that no appreciable decomposition occurs below 110° for oxalic alone, and below 240° for adipic acid alone [3, 4]. When, however, oxalic acid is heated with ethylene glycol for five hours at 110°, about 25% of the acid is decomposed. In the same way, when adipic acid is heated with ethylene glycol, evolution of carbon dioxide is observed already at 150°.

The decomposition of oxalic acid during its reaction with ethylene glycol becomes detectable already at 90°, and it increases greatly with rise of temperature, as can be seen from Fig. 2, in which graphs are shown for the decomposition of oxalic acid at various temperatures. The decomposition of malonic acid at 90° is still more vigorous than that of oxalic acid. It increases with rise in temperature, but not as rapidly as that of oxalic acid, as can be seen clearly from Fig. 3, in which graphs are shown for the decomposition of malonic acid at various temperatures.

In the study of the reactions of ethylene glycol with oxalic and malonic acids under the conditions described, in no case was the formation of macromolecular polyesters observed; the reaction mixture finally obtained contained only the original substances, their decomposition products, and substances formed by the interaction of substances contained in the mixture. Hence, the very low thermal stability of oxalic and malonic acids may be regarded as the main cause of their inability to form polyesters by reaction with ethylene glycol. As a result of the elimination of carboxyl groups, oxalic and malonic acids are converted into formic and acetic acids respectively, and these can give only esters of low molecular weight by reaction with glycols.

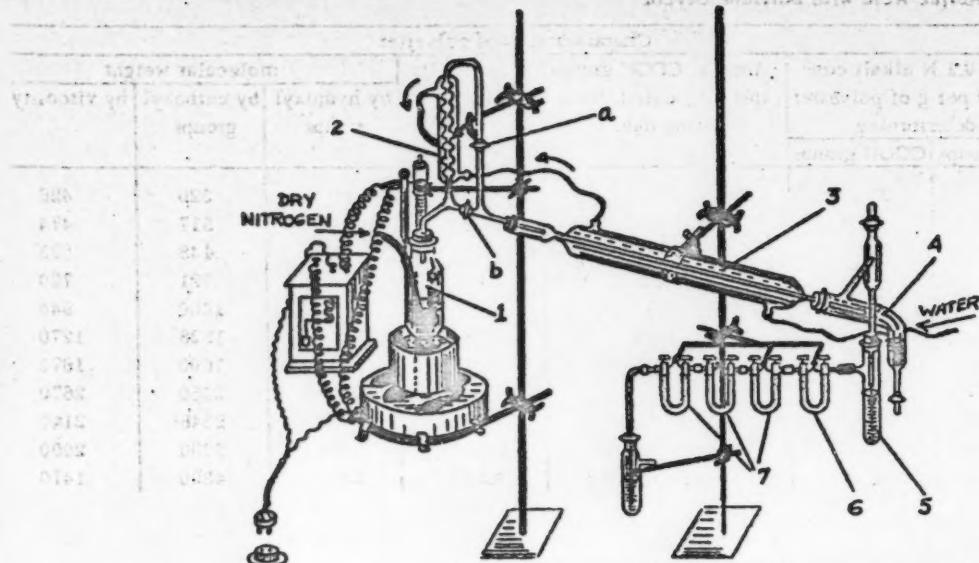


Fig. 1. Diagram of apparatus for the polycondensation of dicarboxylic acids with glycols: 1) condensation tube; 2) reflux condenser; 3) distillation condenser; 4) receiver for reaction water; 5) Drechsel bottle containing concentrated sulfuric acid; 6) calcium chloride U-tube; 7) soda asbestos absorption tubes.

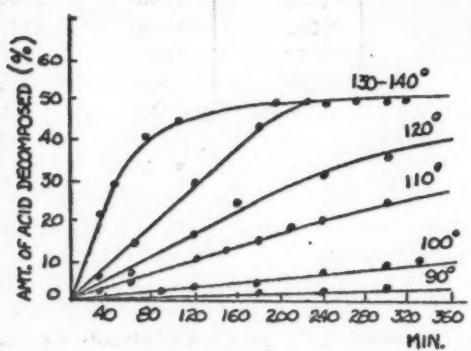


Fig. 2. Decomposition of oxalic acid during polycondensation with ethylene glycol.

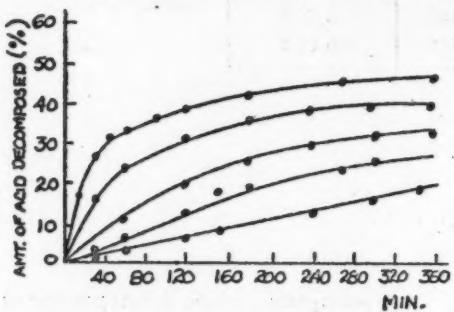


Fig. 3. Decomposition of malonic acid during polycondensation with ethylene glycol.

Succinic, adipic, and sebacic acids are distinguished by considerably higher thermal stabilities, and when heated with ethylene glycol, macroinolecular polyesters are generally formed. The study of the decomposition of these acids was carried out at higher temperatures.

When succinic acid was heated with ethylene glycol, appreciable decomposition of the acid was observed from 240° upward. Fig. 4 shows the increase in the amount of carboxyl groups eliminated with rise in temperature and the variation in the molecular weight of the polyester formed. It is quite obvious in this case that the molecular weight, as determined by carboxyl groups, increases, whereas the molecular weight values determined from viscosity in solution and by hydroxyl groups rises to a maximum and then falls. The explanation of this is that, as a result of decarboxylation, the number of carboxyl groups in the polymer falls, leading to an apparent increase in molecular weight, whereas in actual fact the molecular weight falls, as is shown by viscosity measurements on solutions of the polyester.

In the case of the polycondensation of ethylene glycol with adipic acid, appreciable decomposition of the latter begins at 250°, and it is again manifested by a fall in the molecular weight of the resulting polyester, as determined by viscosity and hydroxyl groups. In contrast to this, the molecular weight determined by carboxyl groups, as in the case of succinic acid, continues to rise, and this is to be explained in the same way as before.

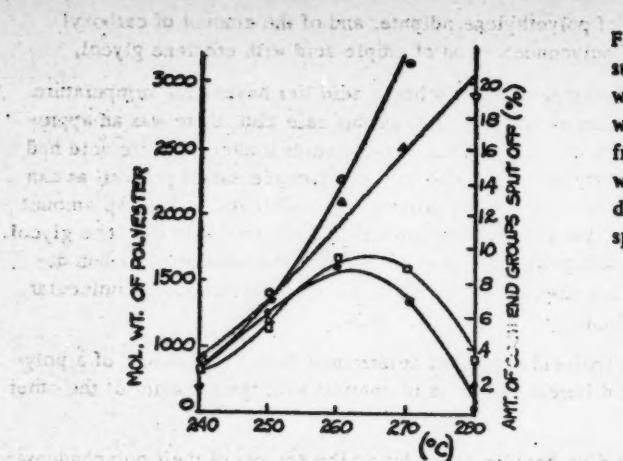


Fig. 4. Variation in the molecular weight of polyethylene succinate, and of the amount of carboxyl groups eliminated, with the temperature of the polycondensation of succinic acid with ethylene glycol: \square = molecular weight determined from the viscosity of a solution of the polyester; \bullet = molecular weight determined by hydroxyl groups; Δ = molecular weight determined by carboxyl groups; \circ = amount of carboxyl groups split off.

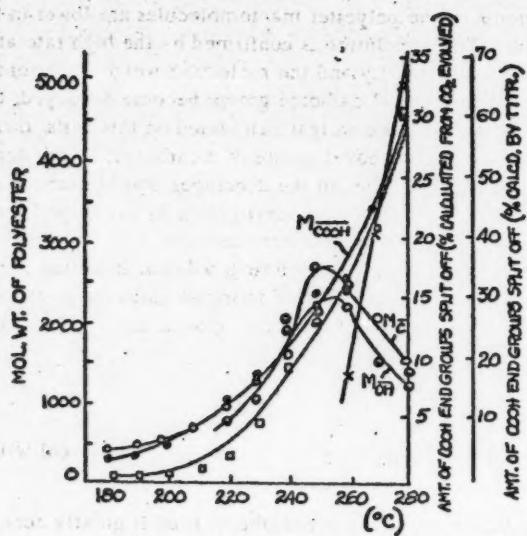


Fig. 5. Variation in the molecular weight of polyethylene adipate, and of the amount of carboxyl groups eliminated, with the temperature of the polycondensation of adipic acid with ethylene glycol: \circ = molecular weight determined from the viscosity of a polyester solution; \bullet = molecular weight determined by hydroxyl groups; \bullet = molecular weight determined by carboxyl groups; \square = amount of carboxyl groups split off, calculated from amount of CO_2 evolved; x = amount of carboxyl groups split off, calculated from titration data.

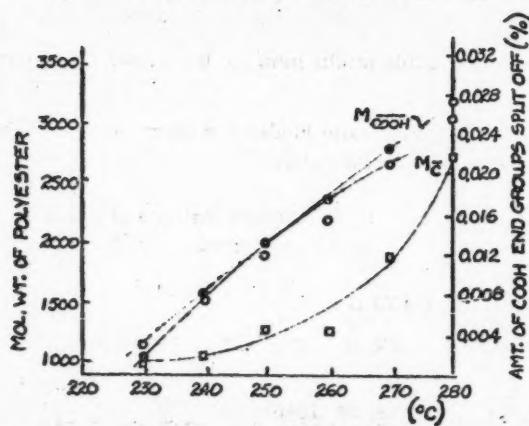


Fig. 6. Variation in the molecular weight of polyethylene sebacate, and of the amount of carboxyl groups eliminated, with the temperature of the polycondensation of sebacic acid with ethylene glycol: \circ = molecular weight determined from the viscosity of a polyester solution; \bullet = molecular weight determined by carboxyl groups; \square = amount of carboxyl groups split off.

Fig. 5 shows the variation of the molecular weight of polyethylene adipate, and of the amount of carboxyl groups eliminated, with change in the temperature of the polycondensation of adipic acid with ethylene glycol.

As we have shown previously [3], the decomposition temperature of sebatic acid lies beyond the temperature range in which its polycondensation with ethylene glycol was carried out, but, in this case also, there was an appreciable amount of carbon dioxide formed at lower temperatures. Of the dicarboxylic acids studied, sebatic acid had the highest thermal stability, and this characteristic was fully preserved also in the polycondensation process, as can be seen from Fig. 6, which shows the variation of the molecular weight of polyethylene sebacate, and of the amount of the carboxyl groups eliminated, with the temperature of the polycondensation of sebatic acid with ethylene glycol. With increase in reaction temperature from 230° to 280°, although there is an increase in the amount of carbon dioxide evolved, this attains only 0.023%, i.e., very much less than for the other acids. For this reason the molecular weight rises continuously over the temperature range studied.

In accordance with this behavior, the values of the molecular weights determined from the viscosity of a polyester solution and by carboxyl groups are not appreciably different, which is in contrast with the behavior of the other dicarboxylic acids studied.

As already noted, in all cases the decomposition of dicarboxylic acids during the process of their polycondensation with glycols occurs at lower temperatures than the decomposition of the acids themselves. We consider that the cause of this phenomenon is that the terminal carboxyl groups of the polyester macromolecules are lower in thermal stability than the carboxyl groups of the dicarboxylic acids. This conclusion is confirmed by the high rate at which the discrepancy between the molecular weight determined from viscosity and the molecular weight determined from carboxyl end groups increases with rise in temperature. As the terminal carboxyl groups become destroyed, their determinable amount naturally becomes less and less, and the molecular weight calculated on this basis, therefore, rises proportionally. If, however, preferential decomposition of the carboxyl groups of dicarboxylic acids occurred, then there would inevitably be an accumulation of hydroxyl groups. Thus, in the decomposition of succinic and sebatic acids the main products are cyclic compounds, and the blocking of hydroxyl groups by decomposition products of the acids cannot occur. In this case the molecular weight determined from terminal hydroxyl groups should be correspondingly less than that determined from the viscosity of a polyester solution, whereas in actual fact the difference between their values was small. On the other hand, the elimination of terminal carboxyl groups with evolution of carbon dioxide leads to the formation of nondeterminable terminal alkyl groups, and such a concept is in accord with the observed facts.

SUMMARY

1. A study has been made of the effect of temperature on the polycondensation of ethylene glycol with oxalic, malonic, succinic, adipic, and sebatic acids.
2. It has been found that in presence of ethylene glycol the process of decarboxylation is greatly accelerated, and as a result no polyester is formed at all in the case of oxalic and malonic acids, and in the case of succinic and adipic acids the molecular weight of the resulting polyester falls as the reaction temperature rises.
3. It has been found that in presence of glycols the decarboxylation temperatures of dicarboxylic acids are greatly lowered.
4. It has been established that the evolution of carbon dioxide results from the breakdown of the terminal carboxyl groups of the polyester molecule.
5. It has been shown that the breakdown of terminal carboxyl groups hinders the normal course of the polycondensation and leads to the formation of polyesters of lower molecular weight.

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MACROMOLECULAR COMPOUNDS

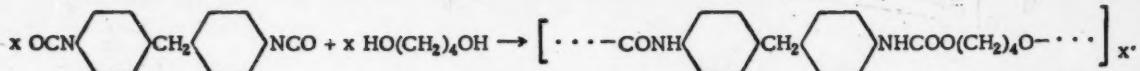
COMMUNICATION 63. EFFECT OF VARIOUS FACTORS ON THE COPOLYMERIZATION OF DIISOCYANATES AND GLYCOLS

V. V. Korshak and I. A. Gribova

As long ago as 1887, Solonitsa discovered for the first time the ability of various monomers to enter into copolymerization reactions [1]. He found that allyl esters and sulfur dioxide were able to copolymerize with the formation of macromolecular compounds, namely the polysulfones [1, 2]. Copolymerization reactions of this sort—sometimes called, not altogether appropriately, heteropolymerization [3]—have not received much investigation, and the laws governing them have not yet been studied in detail. Particularly little study has been devoted to the copolymerization of diisocyanates with glycols, which results in the formation of polyurethans, the polyamidoesters of carboxylic acid [4].

Lieser and Macura [5], Bayer and coworkers [6, 7], and Hochtl [8] have described the conditions for reaction between di- or tri-isocyanates and polyhydric alcohols, and have characterized the properties of the products. Strepikheev, Artemyev, and Shmidt [9] have investigated the effect of the nature of the glycol and solvent and of the proportions of starting materials on the properties of the product of this reaction. As a result of these investigations, much has become known concerning the conditions for the preparation of the products of this reaction, their properties, and their fields of application. But the general picture of the reactions occurring and their mechanism has remained almost without consideration. It was with the object of elucidating these questions that the present investigation was undertaken. Our results have already been published in part [10, 11].

We have studied the reaction of copolymerization between methylenedi-p-phenylene diisocyanate and 1,4-butanediol, the products of which are soluble in nitrobenzene, so that it was possible to carry out the whole process from beginning to end in a homogeneous medium and so avoid the difficulties associated with the investigation of reactions occurring in a heterogeneous system:



First of all we determined the effect of the duration of heating on the specific viscosity of the reaction solution at 145°. A solution of equimolecular amounts of methylenedi-p-phenylene diisocyanate and 1,4-butanediol in nitrobenzene was heated in an Ostwald viscometer, and at definite intervals of time, the time of flow was determined and the specific viscosity of the solution calculated. The results obtained are given in Table 1.

TABLE 1

Change in the Specific Viscosity of the Reaction Solution with Time

Duration of heating (mins.)	Specific viscosity of solution having concentration shown (mole/liter)			
	0.0973	0.151	0.175	0.196
30	0.034	0.085	0.164	0.228
60	0.044	0.137	0.257	0.344
90	—	—	0.351	0.474
120	0.091	0.220	0.433	0.579
180	0.129	0.287	0.591	0.831
240	0.170	0.322	0.690	1.047
300	0.176	0.348	—	1.163
330	—	—	0.790	—
360	0.202	0.363	0.836	Precipitate formed
420	0.228	0.363	—	—

From the data in Table 1 the graphs in Fig. 1 were constructed. They show that for the polymers formed there is an increase in molecular weight with time.

In order to determine the effect of the duration of the reaction on the molecular weight of the polymer formed, experiments were carried out in which test samples were taken at definite intervals of time and their molecular weights determined from viscosity measurements in solution. The results are given in Table 2 (concentration of the diisocyanate 0.352 mole/liter; equimolecular proportions; nitrobenzene solvent).

As can be seen from Fig. 2, the difference in the molecular weights of the products obtained at 145° and at 155° is at first

TABLE 2

Change of Molecular Weight with Time

Duration of heating (min.)	Reaction temperature (°C)			
	145		155	
	specific viscosity of 0.5% solution in 85% phenol	mole weight	specific viscosity of 0.5% solution in 85% phenol	mole weight
30	0.082	55,000	0.105	6,500
60	0.109	6,700	0.134	8,300
90	0.132	8,200	0.153	9,500
180	0.167	10,300	0.212	13,200
240	0.183	11,400	0.252	15,500
300	0.203	12,600	0.244	15,200
360	0.238	14,600	0.259	16,000
420	0.260	16,700	0.266	16,500
480	0.287	17,800	0.245	15,100
600	0.309	19,200	0.253	15,700

such that at the higher temperature a polyurethan of higher molecular weight is formed. After six hours, however, the picture has changed, and the product obtained at the lower temperature has the higher molecular weight. This is evidently associated with the greater prominence at higher temperatures of destructive reactions, which curtail the growth of the molecules.

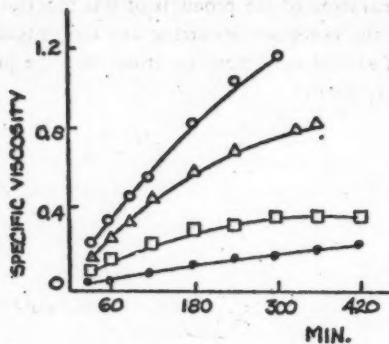


Fig. 1. Dependence of the specific viscosities of reaction solutions of various concentrations on the duration of the reaction: \circ = 0.196 mole/liter; Δ = 0.175 mole/liter; \square = 0.151 mole/liter; \bullet = 0.0973 mole/liter.

equimolecular amounts of the starting materials being heated together for a given time (six hours) in nitrobenzene solution (the amount of nitrobenzene was ten times the total amount of reactants). The results are given in Table 3.

As will be seen from the graph in Fig. 3, the molecular weight is greatly dependent on the reaction temperature for a given time of heating. The products obtained in the temperature range 145-155° have the greatest molecular weight. At lower temperatures, owing to the low reaction rate, the process does not appear to go to completion, and at higher temperatures the part played by destructive reactions comes into prominence, resulting in a fall in the molecular weight of the product.

The above results were obtained for reactions in which the starting materials were taken at one particular concentration. At other concentrations considerable differences in the results may be expected. Experiments were, therefore, performed in which the starting materials, still taken in equimolecular proportions, were taken in concentrations varying from 0.027 to 0.24 g per g of solvent. The reaction was carried out for six hours at 165°. The results are given in Table 4.

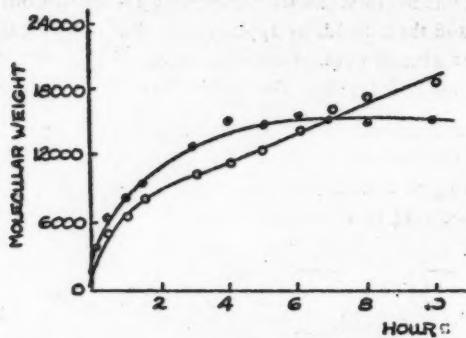


Fig. 2. Dependence of the molecular weights of polyurethans on the duration of the reaction: \bullet = at 155°; \circ = at 145°.

The effect of temperature on the rise in the molecular weights of polyurethans was studied over the range 103-184°, equimolecular amounts of the starting materials being heated together for a given time (six hours) in nitrobenzene solution (the amount of nitrobenzene was ten times the total amount of reactants). The results are given in Table 3.

TABLE 3

Dependence of the Molecular Weight of the Polyurethans on the Reaction Temperature

Reaction temp. (°C)	Properties of polyurethan	
	sp. viscosity of 0.5% soln. in 85% phenol	mole weight
103	0.191	12,000
125	0.231	13,000
140	0.280	17,700
145	0.448	27,000
150	0.425	26,500
155	0.344	21,700
165	0.273	16,100
184	0.181	11,600

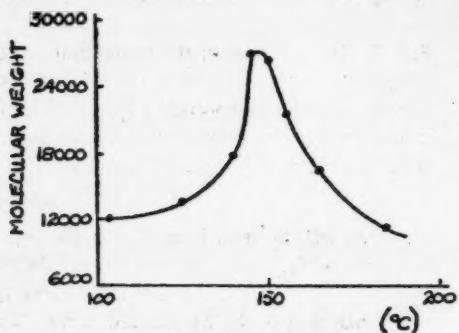


Fig. 3. Dependence of the molecular weight of the polyurethan on the reaction temperature.

TABLE 4

Effect of the Concentration of the Starting Materials on the Molecular Weight of the Polyurethan

Concn. of reactants in soln. (g per g of nitrobenzene)	Sp. viscosity of 0.5% polyurethan in 85% phenol	Mole weight of polyurethan
0.039	0.124	7,700
0.055	0.180	10,800
0.084	0.271	16,100
0.150	0.387	24,300

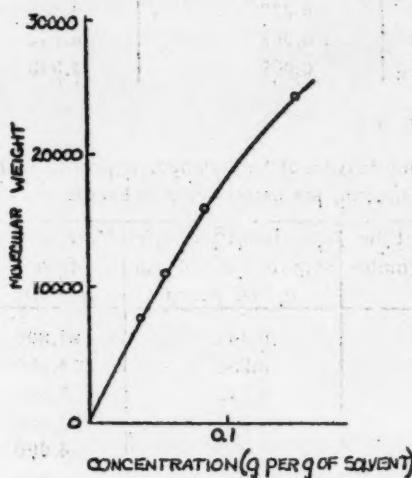


Fig. 4. Dependence of the molecular weight of the polyurethan on the concentration of the reactants in the solution.

For clarity these results are given in the form of a curve in Fig. 4, from which it will be seen that with increase in concentration the molecular weight of the resulting polymer rises. As is well known, this sort of relationship is observed for the radical polymerization of various unsaturated compounds, and is explained by a chain-propagation reaction with participation of solvent molecules [12]. In the case of the copolymerization of diisocyanates with glycols, such a reaction is impossible. The cause of the lower molecular weights of polyurethans obtained in dilute solutions may be, to some extent, the reduced reaction rate resulting from the reduction in the frequency of collisions between reactant molecules, and we may also expect an intensification of side reactions such as the decomposition of butanediol into water and tetrahydrofuran, which will lead to disturbance of the equimolecular ratio of reactants and to proportional reduction in the molecular weight of the polymer, as will be shown below.

The copolymerization reaction between diisocyanates and glycols, like every other reaction in which two components take part, will be sensitive to the proportion of starting materials. One of us has previously shown that in the polycondensation of dicarboxylic acids with diamines [13] and with glycols [14], in the reaction of dihydrazines with dialdehydes [15], and in the polycondensation of dihalo derivatives with aromatic hydrocarbons [16], the molecular weight of the resulting polymer is at its maximum only when the original substances are in equimolecular proportions, and, when one component is in excess, it falls proportional to the amount of this component. Strepikheev, Artemyev, and Shmidt [9] showed that in the case of the copolymerization of hexamethylene diisocyanate with 1,4-butanediol, the polymer of maximum molecular weight is obtained when the original components are in equivalent proportions. The curve that they obtained, however, was unsymmetrical, and this prompted us to verify this relationship for methylenedi-p-phenylene diisocyanate. The reaction was carried out at 145° in a solution containing one part of reactants and ten parts of nitrobenzene. The results are given in Tables 5 and 6.

The results are shown in Fig. 5, in which the continuous line indicates the molecular weight found, and the broken line the molecular weight calculated.

TABLE 5

Copolymerization of 1,4-Butanediol with Methylenedi-p-phenylene Diisocyanate, the Latter being in Excess

Excess of the diisocyanate (mole-%)	Sp. viscosity of 0.5% solution of polyurethane in 85% phenol	Mole weight, from viscosity	Mole weight, calculated*
0.0	0.448	27,000	∞
11.6	0.190	11,900	3,190
17.4	0.113	9,100	2,200
24.3	0.094	5,800	1,650
48.7	0.077	4,800	950
65.4	0.068	4,200	770
100.4	0.069	4,300	590

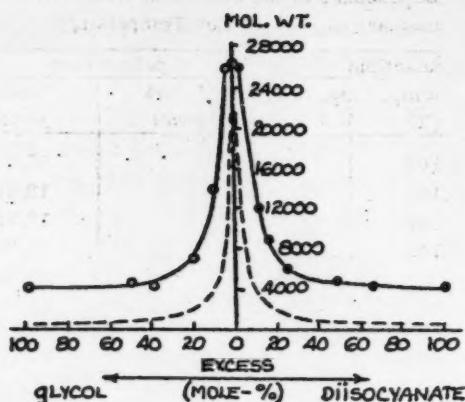


TABLE 6

Copolymerization of Methylenedi-p-phenylene Diisocyanate with 1,4-Butanediol, the Latter being in Excess

Excess of the glycol (mole-%)	Sp. viscosity of 0.5% soln. of polyurethane in 85% phenol	Mole weight, from viscosity	Mole weight, calculated*
0.5	0.442	27,300	68,000
10.7	0.231	14,000	3,260
20.9	0.112	7,000	1,700
40.2	0.069	4,200	930
50.7	0.073	4,600	760
100.9	0.061	3,800	430

Fig. 5. Dependence of the molecular weight of polyurethans on the ratio of original components:
 ----- = molecular weight calculated by formula;
 — = molecular weight determined from viscosity.

As will be seen from Fig. 5, the two branches of the curve are symmetrically arranged and the course of the experimental curve is identical with that of the calculated curve. This indicates that it is possible in principle to calculate the molecular weight of polyurethans beforehand from the excess of one of the components.

An interesting peculiarity of the polyurethans obtained with an excess of diisocyanate is that various values of molecular weight are obtained, depending on the method by which the polymer is isolated. When the solvent is distilled off in steam, polyurethans of higher molecular weight are obtained than when the solvent is removed by washing the resin with alcohol or acetone. Table 7 shows that values of the molecular weight found for polyurethans in the same experiment, in which part of the reaction mixture was treated with alcohol, and part with steam.

These differences in molecular weight probably arise from the fact that the hydrolysis of isocyanate groups yields amino groups, which react with unchanged isocyanate groups. As a result, polyurethans are obtained containing urea groupings in the chain and having a higher molecular weight.



As Strepikheev, Artemyev, and Shmidt [7] showed, diisocyanates react so rapidly with diamines, that the process is reminiscent of ionic reactions and can even occur in an aqueous medium. There is, therefore, nothing surprising in the formation of polyurethan-polyureas that we have found to occur. It is probably to the formation of these that the lack of symmetry of the curve obtained by the above authors must be attributed.

When we had investigated the effect of the proportions of the original reactants on the molecular weight of the polyurethan, there arose the question of how the molecular weight is affected by the addition of a monofunctional substance able to react with isocyanate groups. In order to determine this effect we have investigated the reaction in which the diisocyanate and glycol were taken in equivalent proportions and various amounts of such monofunctional compounds as octyl alcohol and piperidine were added. In other respects the reaction was carried out under the same conditions as before. The results of these experiments are given in Tables 8 and 9.

* The calculated molecular weight was found from the formula:

$$M = \frac{100(M_a + M_b)}{q} + M_a$$

(M_a and M_b are the molecular weights of the original components; q is the excess of the component a in molar percent).

TABLE 7

Effect of the Method of Treatment of the Polyurethan on its Molecular Weight

Expt. No.	Molecular weight of polyurethan treated by	
	washing with alcohol	distilling off solvent in steam
11	15,100	16,900
12	6,600	8,700
15	13,100	21,300

On the basis of these results, the curve in Fig. 6 was constructed.

The results of experiments in which various amounts of piperidine were added are given in Table 9.

TABLE 9

Effect of the Addition of Piperidine on the Molecular Weight of Polyurethan

Amt. of piperidine added (mole-%)	Sp. viscosity of 0.5% soln. of polyurethan in 85% phenol	Mole weight, from viscosity	Mole weight, calculated
0.0	0.450	27,000	∞
2.5	0.162	10,400	13,730
5.1	0.147	8,900	6,770
10.0	0.120	7,200	3,480
20.1	0.075	4,800	1,780
29.4	0.051	3,200	1,220
55.7	0.044	2,800	760

ester linkages in their molecules, and these, as one of us has already shown in collaboration with Zamyatina [17] and with Golubev [14], are readily broken down as the result of aminolysis under the action of diamines, acidolysis under the action of mono- and di-carboxylic acids, and alcoholysis under the action of alcohols, glycols, and other reagents able to react with amide or ester linkages. As a result of these reactions, polyesters and polyamides undergo degradation. Since the polyurethan molecule contains amide and ester linkages, it might be expected that polyurethans would also be degraded under the influence of glycols, acids, amines, and isocyanates, and that this phenomenon occurring in the course of the process should affect the result of the reaction. In order to elucidate this question, we have investigated the action of 1,4-butanediol, adipic acid, aniline, and phenyl isocyanate on polyurethan.

The glycolysis of polyurethan was studied for the product obtained from equimolecular amounts of methylenediphenylene diisocyanate and 1,4-butanediol. This polyurethan was heated with various amounts of 1,4-butanediol in nitrobenzene solution at 170°, and test samples were taken at definite intervals of time; the molecular weights of these were determined from their viscosities (0.5% solution in 85% aqueous phenol). The results are given in Table 10.

On the basis of these results, the curves given in Fig. 8 were constructed; they show the way in which the molecular weight of the polyurethan varies with time when it is heated with various amounts of 1,4-butanediol.

As will be seen from Fig. 8, the degree of degradation rises with increase in the amount of the degrading agent (1,4-butanediol) taken. An important feature of this process is indicated by the fact that, when the polyurethan is heated in nitrobenzene solution in absence of 1,4-butanediol, degradation still occurs, although to an appreciably less extent. In the experiments with 1,4-butanediol, it is probably necessary to take into account also degradation due to thermal action or oxidation by nitrobenzene.

In separate experiments the polyurethan was heated with ten times its weight of ethylene glycol for six hours, and after this degradation treatment its molecular weight was found to be 7670 (originally 26,300). Another sample

TABLE 8

Effect of the Addition of n-Octyl Alcohol on the Molecular Weight of Polyurethan

Amt. of octyl alcohol added (mole-%)	Sp. viscosity of 0.5% soln. of polyurethan in 85% phenol	Mole weight, from viscosity	Mole weight, calculated
0.0	0.428	27,000	∞
0.9	0.163	10,300	37,910
2.0	0.145	9,900	17,130
5.2	0.175	10,800	6,670
10.0	0.106	6,400	3,530
22.6	0.080	4,800	1,630
53.9	0.050	3,100	796

On the basis of these results, the curve in Fig. 7 was constructed. As will be seen from Figs. 6 and 7, the molecular weight of a polyurethan formed in the presence of octyl alcohol or piperidine falls in proportion to the amount of the addition. In this case the addition has the same effect as excess of one of the original components, and leads to reduction in the molecular weight of the polyurethan. The mechanism of the action of the additives investigated may evidently be stated as follows: both alcohols and amines react with terminal isocyanate groups and convert them into groups that are inactive in this reaction, so preventing the further growth of the polymer.

Polyurethans belong to the group of hetero-chain polyamidoesters, and they have amide and

ester linkages in their molecules, and these, as one of us has already shown in collaboration with Zamyatina [17] and with Golubev [14], are readily broken down as the result of aminolysis under the action of diamines, acidolysis under the action of mono- and di-carboxylic acids, and alcoholysis under the action of alcohols, glycols, and other reagents able to react with amide or ester linkages. As a result of these reactions, polyesters and polyamides undergo degradation. Since the polyurethan molecule contains amide and ester linkages, it might be expected that polyurethans would also be degraded under the influence of glycols, acids, amines, and isocyanates, and that this phenomenon occurring in the course of the process should affect the result of the reaction. In order to elucidate this question, we have investigated the action of 1,4-butanediol, adipic acid, aniline, and phenyl isocyanate on polyurethan.

The glycolysis of polyurethan was studied for the product obtained from equimolecular amounts of methylenediphenylene diisocyanate and 1,4-butanediol. This polyurethan was heated with various amounts of 1,4-butanediol in nitrobenzene solution at 170°, and test samples were taken at definite intervals of time; the molecular weights of these were determined from their viscosities (0.5% solution in 85% aqueous phenol). The results are given in Table 10.

On the basis of these results, the curves given in Fig. 8 were constructed; they show the way in which the molecular weight of the polyurethan varies with time when it is heated with various amounts of 1,4-butanediol.

As will be seen from Fig. 8, the degree of degradation rises with increase in the amount of the degrading agent (1,4-butanediol) taken. An important feature of this process is indicated by the fact that, when the polyurethan is heated in nitrobenzene solution in absence of 1,4-butanediol, degradation still occurs, although to an appreciably less extent. In the experiments with 1,4-butanediol, it is probably necessary to take into account also degradation due to thermal action or oxidation by nitrobenzene.

In separate experiments the polyurethan was heated with ten times its weight of ethylene glycol for six hours, and after this degradation treatment its molecular weight was found to be 7670 (originally 26,300). Another sample

of polyurethan of molecular weight 29,300 was heated with ten times its weight of 1,4-butanediol, and its molecular weight fell to 8500.

The tendency of polyurethans to undergo acidolysis was established by heating a sample of polyurethan of molecular weight 29,300 with ten times its weight of adipic acid. After six hours the molecular weight had fallen to 4900.

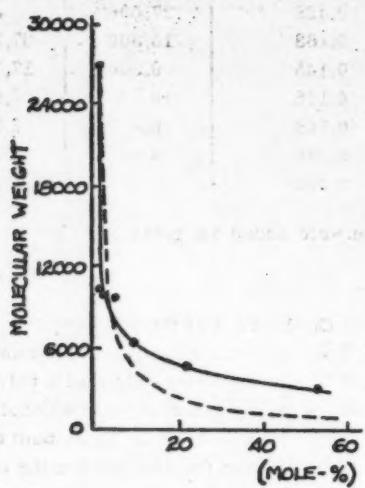


Fig. 6. Effect of additions of octyl alcohol on the molecular weight of the polyurethan: ----- = molecular weight calculated by formula; — = molecular weight determined from viscosity.

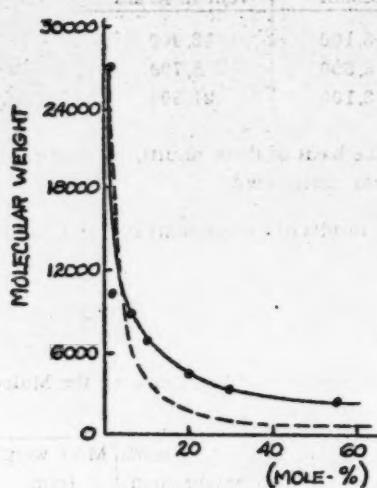


Fig. 7. Effect of additions of piperidine on the molecular weight of the polyurethan: ----- = molecular weight calculated by formula; — = molecular weight determined from viscosity.

TABLE 10

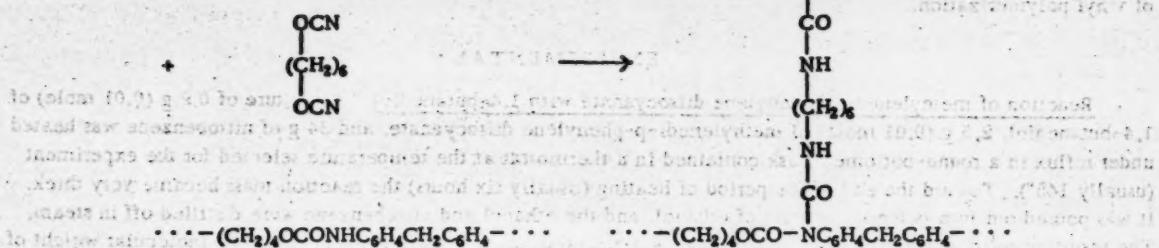
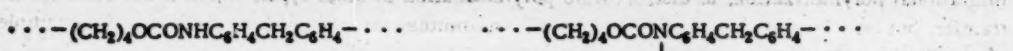
Kinetics of the Degradation of Polyurethan with 1,4-Butanediol

Duration of heating (min)	Control expt.		Addition of 12.4% 1,4-butanediol		Addition of 33.5% 1,4-butanediol		Addition of 50.8% 1,4-butanediol	
	sp. viscosity of 0.5% soln.	mole weight	sp. viscosity of 0.5% soln.	mole weight	sp. viscosity of 0.5% soln.	mole weight	sp. viscosity of 0.5% soln.	mole weight
0.0	0.249	15,600	0.249	15,600	0.249	15,600	0.249	15,600
15	0.201	12,200	—	—	—	—	—	—
30	0.190	11,500	—	—	—	—	—	—
60	0.164	10,200	0.157	10,000	0.141	8,600	0.139	8,400
120	0.164	10,200	0.142	8,000	0.134	8,200	—	—
180	0.159	10,100	0.141	8,700	0.123	7,700	—	—
240	—	—	—	—	5.109	6,700	0.083	5,200
300	0.168	10,500	0.129	7,900	0.110	6,700	—	—
360	—	—	0.122	7,800	—	—	—	—

The aminolysis of polyurethans was carried out by heating a sample of polyurethan with aniline for six hours; the molecular weight fell from 26,000 to 2800. The isocyanolysis of polyurethan was carried out by heating it with phenyl isocyanate. The polyurethan dissolved completely, and no precipitate was formed when the solution was poured into benzene, evidently because the macromolecules had been completely destroyed and converted into a product of low molecular weight.

Attempts to effect isocyanolysis by means of hexamethylene diisocyanate resulted in the formation of an infusible insoluble product, whose molecular weight could not be determined. It may be supposed that in this case, in addition to degradation, there occurred cross-linking of the polyurethan macromolecules with formation of a three-dimensional product, which, like all compounds of that type, was infusible and insoluble. Such cross-linking may

occur as a result of the reaction of hexamethylene diisocyanate with hydrogens of amide groups in accordance with the scheme:



In order to make sure that such a reaction is possible, we examined the possibility of a process of this type in the case of the reaction of methylenedi-p-phenylene diisocyanate with 6-caprolactam (2-oxohexamethyleneimine).

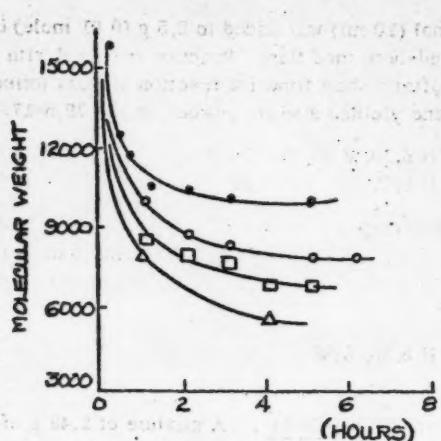


Fig. 8. Degradation of polyurethan in presence of 1,4-butanediol: $\Delta = 50.8$ mole-% excess of 1,4-butanediol; $\square = 33.5$ mole-% excess of 1,4-butanediol; $\circ = 12.4$ mole-% excess of 1,4-butanediol; \bullet = in absence of 1,4-butanediol.

hol, carboxyl, amine, or isocyanate groups in their molecules. We may conclude from this that such degradative reactions play a determining part also in the course of the synthesis of polyurethans by the copolymerization of diisocyanates with glycols.

In conclusion, we will discuss briefly the general characteristics of the reaction of diisocyanates with glycols leading to the formation of polyurethans. This reaction must be classified as a polymerization reaction, mainly by the criterion of the absence of elimination of a low-molecular-weight product, which is characteristic of a polycondensation process. At the same time, this reaction differs in principle from radical and ionic polymerizations, which are typical for various vinyl monomers and require the participation of initiators or catalysts. It differs essentially also from hydrolytic polymerization [18], which is characteristic for cyclic esters and amides, such as 6-caprolactam, which for their polymerization require activators such as water, acids, amines, alcohols, and similar substances having mobile hydrogen atoms [19].

The peculiarity of the copolymerization reaction between diisocyanates and glycols is the occurrence of hydrogen transfer at each stage of the process, in accordance with the scheme:



It is not, however, a chain reaction, since no free radicals take part in the intermediate stages, and the reaction is not initiated by peroxides and other generators of free radicals. Since we have a stable compound at every stage of the reaction and observe a continuous rise in molecular weight during the course of the reaction, we have sufficient grounds to classify this reaction as a multistage reaction.

Polymeric reactions of this type, which are associated with transfer of a hydrogen atom, may be called migrational polymerization, as distinct from polymerization of other types, which is not accompanied by hydrogen transfer, but only by the opening of double bonds and mutual saturation of valencies, as, for example, in the case of vinyl polymerization.

EXPERIMENTAL

Reaction of methylenedi-p-phenylene diisocyanate with 1,4-butanediol. A mixture of 0.9 g (0.01 mole) of 1,4-butanediol, 2.5 g (0.01 mole) of methylenedi-p-phenylene diisocyanate, and 34 g of nitrobenzene was heated under reflux in a round-bottomed flask contained in a thermostat at the temperature selected for the experiment (usually 145°). Toward the end of the period of heating (usually six hours) the reaction mass became very thick. It was poured out into twice its volume of ethanol, and the ethanol and nitrobenzene were distilled off in steam. The resulting solid was filtered off, washed with water, and dried in a thermostat at 70°. The molecular weight of the resin was determined from the viscosity of a 0.5% solution in 85% aqueous phenol. The resulting polyurethane was a white or slightly pink powder, m.p. 190-200°, readily soluble in cresol and 85% aqueous phenol, and insoluble in the usual organic solvents.

Dimethyl(methylenedi-p-phenylene)dicarbamate. Methanol (10 ml) was added to 2.5 g (0.01 mole) of methylenedi-p-phenylene diisocyanate contained in a 50-ml round-bottomed flask. Reaction occurred with the evolution of much heat. The mixture was allowed to stand, and after a short time the reaction product formed a precipitate, and was filtered off. Recrystallization from hot toluene yielded a white powder, m.p. 178.5-179.5°.

Found %: C 65.71; 65.86; H 6.13; 6.00; N 9.04; 9.25
 $C_{17}H_{18}O_4N_2$. Calculated %: C 64.95; H 5.77; N 8.92

Diphenyl (methylenedi-p-phenylene)dicarbamate. Methylenedi-p-phenylene diisocyanate (3.48 g) was mixed with phenol (2.7 g) in a round-bottomed flask, and 10 ml of dry toluene was added. The mixture was heated at the boil for three hours and then allowed to cool to room temperature. Recrystallization of the resulting precipitate from hot toluene yielded a white powder, m.p. 168°.

Found %: C 74.47; 74.52; H 5.35; 5.38
 $C_{27}H_{22}N_2O_4$. Calculated %: C 73.95; H 5.05

1,1'-(Methylenedi-p-phenylene)dicarbamoyl]bis(2-oxohexamethyleneimine). A mixture of 2.48 g of methylenedi-p-phenylene diisocyanate and 2.25 g of 6-caprolactam was heated at 145° for three hours. Toward the end of this time the reaction mixture generally solidified. The product was recrystallized from hot benzene, and yielded a white powder, m.p. 174-175°.

Found %: C 68.29; 67.90; H 6.83; 7.22
 $C_{27}H_{32}N_4O_4$. Calculated %: C 68.02; H 6.77

SUMMARY

1. A study has been made of the effect of time, temperature, concentration, ratio of original components, and addition of monofunctional compounds on the rise in molecular weight of polyurethans formed by copolymerization of methylenedi-p-phenylene diisocyanate with 1,4-butanediol. The properties of the products formed have been examined.
2. It has been shown that the molecular weight of the polyurethans increases continuously as the duration of reaction increases.
3. It has been found that the molecular weight of the polyurethans attains a maximum value in a definite temperature range; at lower or higher temperatures the molecular weight falls.
4. It has been shown that, with rise in the concentration of the solution, the molecular weight of the polyurethans rises. An explanation has been given for this phenomenon.
5. It has been shown that the dependence of the molecular weight of the polyurethans on the ratio of original components is expressed by a symmetrical curve.
6. It has been found that additions of monofunctional substances bring about a reduction in the molecular weight of the polymer obtained.
7. The possibility of obtaining mixed polyurethane-polyureas has been demonstrated.

8. It has been found that polyurethans undergo alcoholysis in presence of glycols, aminolysis in presence of amines, acidolysis in presence of acids, and isocyanolysis in presence of isocyanates. All of these reactions result in the degradation of the polymer.

9. It has been shown that isocyanates are able to react with amides, the example taken being the reaction of methylenedi-p-phenylene diisocyanate with 6-caprolactam, and an explanation has been advanced for the formation of three-dimensional products when hexamethylene diisocyanate reacts with a polyurethan.

10. The peculiarities of the copolymerization of diisocyanates with glycols have been discussed, and it is proposed that these reactions should be regarded as a new type of polymerization, namely migrational polymerization.

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of solvent and most molecules. Now such a large and significant role belongs to spectroscopy and all GPC's of the methods used.

S. B. KAT

BRIEF COMMUNICATIONS

Some investigations on the synthesis of the substances in question are given in the

present article.

DIPOLE MOMENTS OF SOME INTERMEDIATE PRODUCTS IN THE

SYNTHESIS OF VITAMIN A

V. M. Kazakova, Ya. K. Syrkin, and A. N. Shidlovskaya

We have determined the dipole moments of some β -ionone derivatives that form intermediate products in the synthesis of vitamin A. The dielectric constants were measured by the heterodyne method in benzene solution at 25°. Table 1 gives the constants of the substances investigated, extrapolated to infinite dilution: the total polarization P , the refraction for the yellow line of sodium (R_{Na}), the orientation polarization, and, in the last column, the dipole moment. For two of the substances the refraction was measured for six wave lengths, and the value of λ_{∞} was found and the exaltation of refraction calculated; the results are given in Table 2. We measured the refraction of the ethyl ester of 5-methyl-7-(2,6,6-trimethyl-1-cyclohexen-1-yl)-2,4,6-heptatrienoic acid. We assumed that the exaltation of refraction for the methyl ester and for the acid itself would be approximately the same as for the ethyl ester (4.5 cm for the extrapolated value and 6.7 for R_{Na}). On this basis the refractions of the corresponding substances were determined.

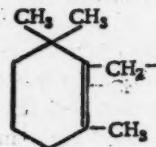
TABLE 1

Substance	B.p. in °C (p in mm Hg)	P_{∞}	R_{Na}	P_{Or}	$\mu \cdot 10^{16}$
β -Ionone 	80 (0.1)	313.4	61.7	251.7	3.47
α ,2,6,6-Tetramethyl-1-cyclohexene-1-crotonaldehyde (Aldehyde C ₁₄) 	95 (0.3)	331.3	67.2	264.1	3.56
3-Methyl-5-(2,6,6-trimethyl-1-cyclohexen-1-yl)-2,4-pentadien-1-ol (Alcohol C ₁₅) 	100 (10 ⁻³)	161.7	70.7	91	2.09
5-Methyl-7-(2,6,6-trimethyl-1-cyclohexen-1-yl)-2,4,6-heptatrienoic acid 	B.p. 158-159°	257.1	87.1	170.0	2.85
Methyl ester of 5-methyl-7-(2,6,6-trimethyl-1-cyclohexen-1-yl)-2,4,6-heptatrienoic acid 	125 (10 ⁻³)	267.9	90.6	177.3	2.92

TABLE 2

Wavelength	Alcohol C ₁₅	Aldehyde C ₁₄
Cd orange 6438.47	69.10	66.94
Hg yellow 5790.66	70.87	67.25
Hg green 5460.71	71.17	67.60
Cd green 5085.82	71.88	67.86
Cd blue 4799.91	72.38	68.19
Cd blue 4678.15	72.53	68.54
R _∞ extrapolated	67.3	63.5
R _∞ additive		
ΔR	0.6	1.8

As is well known, transition from formaldehyde to acetaldehyde is accompanied by an appreciable increase in dipole moment (from 2.27 to 2.72 D (in the vapor)). This is associated with increase in the negative charge on the oxygen at the expense of the hydrogens of the methyl group. It is further known that the conjugation of the carbonyl bond with the double bond C=C also leads to a considerable rise in the moment. Thus, in benzene solution acrolein has a moment of 2.28 D and methacrylaldehyde a moment of 2.72 D, which is considerably higher than that of acetaldehyde in solution (2.56 D). In the substances that we have investigated, these regularities are manifested more strongly. In Aldehyde C₁₄, the moment is considerably enhanced in comparison with methacrylaldehyde (3.58 instead of 2.72 D). In this we have a hydrogen of methacrylaldehyde replaced by an apparently nonpolar group.



The moment of Alcohol C₁₅ (2.09 D in solution) is higher than that of allyl alcohol (1.63 D in the vapor). Whereas the polarity of allyl alcohol with its one double bond does not differ from that of the usual alcohols, the presence of the additional double bond and methyl group in Alcohol C₁₅ results in an appreciable increase in moment. The dipole moments of formic and acetic esters (from methyl to pentyl) lie in the range 1.8-1.9 D. The introduction of a chain of four conjugated C=C bonds leads to an increase in moment of about 1 D. It should be noted that acids in the dimeric state have reduced moments. In our case, at concentrations of about 0.0015, the moment of 5-methyl-7-(2,6,6-trimethyl-1-cyclohexen-1-yl)-2,4,6-heptatrienoic acid is 2.85 D. It will be seen that the moment of this molecule is greater by about 1.2 D than the moments of monomeric acids that do not contain a double bond.

The authors express their gratitude to G. I. Samokhvalov for providing the preparations investigated.

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MOLAR REFRACTIONS AT VARIOUS WAVELENGTHS OF SUBSTANCES
HAVING CONJUGATED BOND SYSTEMS

G. G. Kikina, Ya. K. Syrkin, and E. A. Shott-Lyova

Refraction, as is well-known, is a property for which additivity rules are satisfactorily obeyed. In order to elucidate the significance of departures from additivity, it is necessary to know the refraction extrapolated to infinitely long waves. For this purpose the refractive index must be measured at various wavelengths, and extrapolation must then be performed by a well-known formula in order to find R_{∞} . We have made measurements on eight substances (benzene, naphthalene, anthracene, phenanthrene, acenaphthene, triphenylmethane, p-benzoquinone, and phenanthrenequinone) at seven wavelengths, from 4046.56 to 6439.47 Å. In the table we give the wavelength (first column), values of the refraction for the various substances at the various wavelengths, the extrapolated values of

Wavelength Å	Refraction of							
	benzene	naphthalene	anthracene	phenanthrene	acenaphthene	triphenylmethane	p-benzoquinone	phenanthrenequinone
4046.56	27.41	47.56	74.85	68.98	56.11	85.47		
Hg violet								
4678.15	26.75	46.54	70.58	67.42	54.77	83.43		
Cd blue								
4799.91	26.57	46.29	70.15	67.16	54.47	83.02		
Cd blue								
5085.82	26.47	45.66	68.97	66.01	53.75	82.46	30.06	
Cd green								
5460.74	26.27	55.17	67.68	65.12	53.15	81.83	29.67	75.74
Hg green								
5790.66	26.12	44.77	66.97	64.54	52.67	81.45	29.42	74.59
Hg yellow								
6439.47	25.90	44.18	65.50	63.45	52.03	80.80	29.02	72.71
R_{∞}	25.01	41.85	61.01	59.50	49.22	78.06	27.45	66.04
R_{∞} additive	25.28	40.00	54.72	54.72	46.89	76.09	25.87	55.31
ΔR	-0.27	1.85	6.29	4.78	2.33	1.97	1.58	10.73

the refraction (third line from the bottom), the additive values of the refraction extrapolated to infinitely long wavelength, and finally the difference $R_{\infty} - R_{\infty}$ add = ΔR , i.e., the exaltation of refraction calculated by a comparison of R_{∞} with the additive value for λ_{∞} the following values were assumed: H 1.068, C 2.373, double bond 1.546, carbonyl oxygen 2.134. For molecules without conjugated bonds these values are correct within 0.015.

The experimental results indicate a rapid rise in ΔR with increase in the number of conjugated C=C bonds, as will be seen from a comparison of naphthalene with anthracene and p-benzoquinone with phenanthrenequinone. Distortion of valency angles and change in interatomic distances affects ΔR . This follows from a comparison of naphthalene with acenaphthene. "Acenes" and "phenes" having the same number of CC bonds apparently have different ΔR values. This is indicated by a comparison of anthracene and phenanthrene. It is interesting that in triphenylmethane, in spite of the apparent absence of conjugation between the phenyl groups, the exaltation is considerably greater than in benzene. Substances of quinone structure have a high exaltation of refraction. Attention is drawn to the symbiotic relationship between the enhanced exaltations of refraction and the low excitation energies of the triplet state [1].

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SYNTHESIS OF THIOPHENE DERIVATIVES CONTAINING THE
tert-BUTYL GROUP, AND SOME OF THEIR PROPERTIES

Ya. L. Goldfarb and I. S. Korsakova

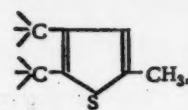
As is well known, the method of alkylation by means of alkyl halides in presence of catalysts of the aluminum chloride type is of little use for the preparation of thiophene homologs from unsubstituted thiophene [1]. An exception is formed by the formation of 2,5-di-tert-butylthiophene in good yield (about 80%) by the action of tert-butyl chloride on thiophene in presence of a catalytic amount of ferric chloride [2]. It would appear that, in this case, the rate of alkylation of thiophene is considerably higher than that of its polymerization, which is promoted by catalysts of this type and is often accompanied by far-reaching breakdown of the thiophene.

In the course of investigations that we are carrying out on thiophene derivatives, the need arose for substituted thiophenes containing a tert-butyl group in the 5-position of the thiophene ring. For their synthesis we have used the method already tried for unsubstituted thiophene of alkylation with tert-butyl chloride in presence of ferric chloride. The mixtures formed by the action of tert-butyl chloride and monosubstituted (2-methyl- and 2-ethyl-) thiophenes consisted mainly of mono- and di-tert-butylated products. The alkylation products were separated by vacuum fractionation, followed sometimes by distillation at atmospheric pressure.

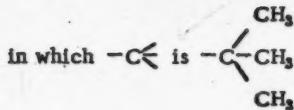
From tert-butyldimethylthiophene (formed under the conditions indicated from 2-methylthiophene) an aldehyde was prepared by the method described by Messina [3], and it gave a semicarbazone of m.p. 215°. According to the results of this investigator, the melting point of the semicarbazone of 5-tert-butyl-2-thiophenecarboxaldehyde is 215-216°. It may, therefore, be presumed that, when tert-butyl chloride reacts with 2-methylthiophene in presence of ferric chloride, substitution occurs in the 5-position. Of the two possible structures (I and II)



(I)



(II)



the di-tert-butylation product of 2-methylthiophene must be assigned the structure I, since the formation of a product of structure II by the alkylation under these conditions of 2-tert-butyl-5-methylthiophene is improbable owing to steric hindrance.

In this connection it should be noted that among the reaction products from thiophene or 2,5-dimethylthiophene and a large excess of tert-butyl chloride in presence of ferric chloride no tri-, or, still more, tetra-substituted thiophenes could be isolated. Finally, if we may seek a parallel in the benzene series, we may mention that o-di-tert-butylbenzene has not been described.

Brown and coworkers [4], in a number of recently published papers on "sterically strained" systems, have come to the conclusion that the preparation of this hydrocarbon by the Friedel-Crafts method is impossible.

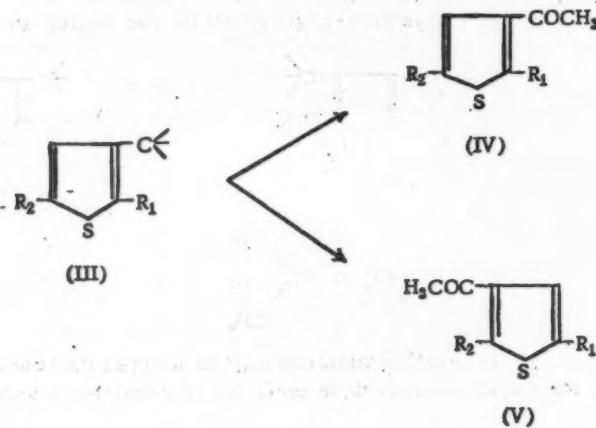
The alkylation of 2-ethylthiophene with tert-butyl chloride in presence of ferric chloride leads, as in the case of 2-methylthiophene, to the formation of two compounds. Judging from their compositions, and taking the results on the alkylation of 2-methylthiophene into account, we may assign the structures of 2-tert-butyl-5-ethylthiophene and 3,5-di-tert-butyl-2-ethylthiophene to these compounds. Alkylation of 2,5-dimethyl- or 2,5-diethyl-thiophene with tert-butyl chloride under the conditions already indicated gives only one product, containing one tert-butyl group (3-tert-butyl-2,5-dimethylthiophene or 3-tert-butyl-2,5-diethylthiophene) in high yield (90-95%).

Since they are trisubstituted thiophenes, these compounds should acylate in the β -position with formation of fully substituted thiophenes. However, when the ketone formed by the action of acetyl chloride on 3-tert-butyl-2,5-dimethylthiophene in presence of stannic chloride was investigated, it was found that it corresponded in composition to the formula $C_8H_{14}OS$, whereas for the "normal" course of the process a ketone of composition $C_{12}H_{16}OS$ should be formed. This fact can only be explained on the assumption that a tert-butyl group is eliminated when acetyl chloride acts on 3-tert-butyl-2,5-dimethylthiophene under our conditions (see experimental part).

When this process was studied further it was found that the ketone formed was, in fact, identical with the ketone that we prepared by the acetylation of 2,5-dimethylthiophene, which we established by comparison of the melting points of the oximes. Our experiments showed that similar elimination of a tert-butyl group occurred in the acetylation in presence of stannic chloride of other trisubstituted thiophenes containing a tert-butyl group that we prepared, namely, 3-tert-butyl-2,5-diethylthiophene, 3,5-di-tert-butyl-2-methylthiophene, and 3,5-di-tert-butyl-2-ethylthiophene, which yielded, respectively, 2,5-diethyl-3-thienyl methyl ketone, 5-tert-butyl-2-methyl-3-thienyl methyl ketone, and 5-tert-butyl-2-ethyl-3-thienyl methyl ketone. In all of these cases the tert-butyl group was eliminated from the β -position, which is evident from the fact that the ketones formed were found to be identical with the ketones obtained from the corresponding α, α' -disubstituted thiophenes (Table 2). In these cases also, the identity of the ketones was established by a comparison of the melting points of the corresponding derivatives and by mixture melting point tests.

Our observation concerning the elimination of the tert-butyl group from the β -position is in accord with the fact that, in the acetylation of 2,5-di-tert-butylthiophene [2] and 2-tert-butyl-5-methylthiophene, the elimination of a tert-butyl group does not occur. The elimination of a tert-butyl group in the acetylation of a system similar in nature to thiophene was recently described by Taylor and Watts [5, 6]: they found that, when p-tert-butyltoluene was treated with acetic anhydride in presence of aluminum chloride, 4'-methylacetophenone was obtained, as a result of the elimination of the tert-butyl group.

At present we do not have all of the experimental data available to enable us to make a choice between the structures IV and V for the ketones formed by the acetylation of systems of the type III:



A knowledge of the structure of these ketones, however, would enable us to make an approach to the understanding of the question, very interesting from the theoretical point of view, of the mechanism of the process of elimination of a tert-butyl group. The formation of the structure IV would indicate that direct elimination of the tert-butyl group by the CH_3CO group occurs, whereas the formation of the isomer V could be regarded as the result of attack by the CH_3CO group in the 4-position with subsequent or simultaneous elimination of the tert-butyl group.

It may be supposed that the first of these elimination processes is the more probable. This assumption of ours is in accord with the observations of Chichibabin [7], who showed that in eliminating an acetyl group a nitro group always takes up the position occupied by that acetyl group, the example that he studied being the nitration of 4'-tert-butyl-2',6'-dimethylacetophenone.

EXPERIMENTAL

Alkylation

Thiophene or its homolog was dissolved in carbon disulfide, and to this solution tert-butyl chloride and ferric chloride were added (for amounts of reactants see Table 1). The dark-brown solution was boiled and stirred for 15-20

TABLE 1

Original substance	Amount of original substance chloride (g and (moles))	Amount of tert-butyl solvent (CS ₂) (ml)	Compound obtained	B.P. in °C (p in mm Hg)	Yield (%)	Analysis					
						C calcd found calcd lated	H calcd found calcd lated	S calcd found calcd lated	n ^D d ₄ ²⁰		
2-Methylthiophene *	30.0 (0.3)	60.0 (0.6)	170	2-tert-Butyl-5-methylthio- phenе**	185.5-186.5 104 (11) 238-239	25 60	70.13 74.28	70.04 70.16 74.10 10.43	9.13 9.06 20.78 15.23	20.69 20.90 1.4972 15.50	0.9391
2-Ethylthiophene	33.6 (0.3)	60.0 (0.6)	150	2-tert-Butyl-5-ethylthio- phenе	78-81 (10) 114-115 (9)	19	71.5 71.37	71.71 9.5 75.29 10.71	9.48 9.43 10.77 10.90	19.21 18.93	1.4966 0.9316
2,5-Dimethylthiophene	30.6 (0.3)	30.0 (0.6)	150	3-tert-Butyl-2,5-dimethyl- thiophene	94-95.5 (21)	92	71.43 71.71 9.52 71.91	71.71 9.52 9.62 9.77	14.46 14.29 14.02	1.5009 0.9255	
2,5-Diethylthiophene	15.8	16.0	70	3-tert-Butyl-2,5-diethyl- thiophene	110-111 (12) 235.5-236.5	85.5	73.47 73.58	73.58 10.20 10.09	10.03 16.33 16.27	16.25 16.33 16.27	1.6050 0.9392

* In each experiment the amount of ferric chloride taken was 0.02-0.04 mole.

** This fraction was treated with N-bromosuccinimide [3] in presence of benzoyl peroxide; from the resulting substance the salt with hexamethylene diamine was formed, and the decomposition of this with steam yielded an aldehyde, the semicarbazone of which melted, after recrystallization from alcohol, at 215°.

For the m.p. of the semicarbazone of 5-tert-butyl-2-thiophene carboxaldehyde, the literature [3] gives 215-216°. Analysis of the semicarbazone: Found % C 53.47; 53.58; H 6.68; 6.63; S 13.75; 13.88; Calculated % C 53.33; H 6.66; S 14.92.

TABLE 2

Starting substance	Ketone obtained	Yield (%)	B.p. in °C (P in mm Hg)	M.p. of derivative (°C)	Composition of derivative	Analysis					
						C calcu- lated	C found	H calcu- lated	H found		
2,5-Dimethylthiophene	2,5-Dimethyl-3-thienyl methyl ketone*	99	108.5-109 (12.5)	A 82-83**	$C_8H_{11}NO$ A	56.80	—	6.55	—	18.95	—
3-tert-Butyl-2,5-dimethylthiophene	2,5-Dimethyl-3-thienyl methyl ketone	56	103.5-106 (11)	A 82-83	$C_8H_{11}NO$ A	—	56.87	—	6.42	—	19.00
2,5-Dimethylthiophene	2,5-Diethyl-3-thienyl methyl ketone***	76	123-124 (11.5)	B 167-168 C 147-148	$C_{11}H_{17}N_3OS$ B	55.23	—	7.11	—	13.38	—
3-tert-Butyl-2,5-diethylthiophene	2,5-Diethyl-3-thienyl methyl ketone	45	123-124 (11)	B 167-168 C 147-148	$C_{11}H_{17}N_3OS$ B	—	55.61	—	7.21	—	13.15
2-tert-Butyl-5-methylthiophene	5(or 2)-tert-Butyl-2(or 5)-methyl-3-thienyl methyl ketone	86	122-122.5 (1.0)	B 219-220 C 158.5-159.5	$C_{11}H_{19}O_2N_4S$ C	54.25	—	5.36	—	8.50	—
3,5-Di-tert-butyl-2-methylthiophene	5(or 2)-tert-Butyl-2(or 5)-methyl-3-thienyl methyl ketone	63	123-124 (11)	B 219-220*** C 158-159	$C_{11}H_{21}O_2N_4S$ C	—	53.30	—	5.42	—	8.76
2-tert-Butyl-5-ethylthiophene	5(or 2)-tert-Butyl-2(or 5)-ethyl-3-thienyl methyl ketone	86	127-128 (9)	B 175 C 152-153	$C_{13}H_{21}N_3OS$ B	58.43	—	7.86	—	11.99	—
2,5-Di-tert-butyl-2-ethylthiophene	5(or 2)-tert-Butyl-2(or 5)-ethyl-3-thienyl methyl ketone	55.5	129-129.5 (1.0)	B 177 C 152-153	$C_{13}H_{21}N_3OS$ B	—	58.89	—	7.86	—	12.15
						—	58.58	—	7.82	—	11.75

A = oxime; B = semicarbazone; C = 2,4-dinitrophenylhydrazone

* Literature [8] gives b.p. 125-128° (28 mm).

** Literature [9] gives m.p. 83°.

*** Literature [10] gives b.p. 126-128° (12 mm), m.p. of semicarbazone 167°.

**** With rapid heating, and m.p. 214-215° with slow heating.

hours, until the evolution of hydrogen chloride almost ceased. The dark-colored reaction mixture was then cooled with ice and decomposed by stirring with water. The solution then became yellow; there was a certain amount of resin on the bottom of the flask. The carbon disulfide layer was separated and washed with 10% HCl, 10% NaOH, and water. The washing waters and the original aqueous layer were extracted with ether, and the ether extract was washed and added to the carbon disulfide solution. The solution was dried over CaCl_2 , the solvent was distilled off, and the residue was vacuum-fractionated and then, if necessary, distilled under atmospheric pressure. The results are given in Table 1.

Acetylation

To a well stirred and ice-cooled (to 0°) solution of the alkylthiophene and acetyl chloride (excess over the theoretical amount of 0.1 of a molecular proportion) in benzene (1:10), a solution of an equimolecular amount of stannic chloride in benzene (1:1) was added carefully and dropwise, at such a rate that the temperature in the flask did not rise above 0°. As soon as the first drops of stannic chloride were added, the solution became red, or sometimes orange. When the whole of the stannic chloride had been added, the dark-red reaction mixture was stirred at room temperature for 4-5 hours. It was then cooled externally with snow, and decomposed by dropwise addition of acidified water (3 ml of concentrated HCl in 30 ml of water). The solution then became yellow. The benzene layer was separated, washed with 10% solutions of HCl and sodium carbonate, washed with water, and dried over calcined MgSO_4 . The benzene was distilled off, and the residue was vacuum-fractionated. The results are given in Table 2.

SUMMARY

1. The conditions have been determined for the alkylation with tert-butyl chloride of 2-methylthiophene, 2-ethylthiophene, 2,5-dimethylthiophene, and 2,5-diethylthiophene, and as a result the following compounds have been synthesized: 2-tert-butyl-5-methylthiophene, 2-tert-butyl-5-ethylthiophene, 3,5-di-tert-butyl-2-methylthiophene, 3,5-di-tert-butyl-2-ethylthiophene, 3-tert-butyl-2,5-dimethylthiophene, and 3-tert-butyl-2,5-diethylthiophene. The alkyl-substituted thiophenes were obtained in 85-95% yields.
2. The structures of these new tert-butyl-substituted thiophenes have been proved by acetylation in presence of stannic chloride.
3. It has been shown for the first time that, in the acetylation in presence of stannic chloride of trisubstituted thiophenes containing a tert-butyl group, the latter is eliminated when it occurs in the β -position.
4. 5-tert-Butyl-2-methyl-3-thienyl methyl ketone and 5-tert-butyl-2-ethyl-3-thienyl methyl ketone have been synthesized.

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C U R R E N T E V E N T S

CONFERENCE ON THE THEORY OF THE STRUCTURE OF GLASS

From November 23 to 27, 1953, a conference was held in Leningrad on the theory of the structure of glass; it was convened conjointly by the Institute of Silicate Chemistry of the USSR Academy of Sciences, the All-Union Scientific Engineering and Technical Society of the Silicate Industry, and the S. I. Vavilov State Optical Institute of the Order of Lenin.

More than five hundred people took part in the conference; they represented about a hundred organizations (research institutes, higher-education establishments, industrial concerns, and ministries), and had traveled from twenty-eight cities.

Thirteen papers were read, and there were seventeen short speeches. About fifty people joined in the discussions.

After a short introductory address by Academician A. A. Lebedev, Prof. K. S. Evstropyev read a paper on the "Crystallite Theory of the Structure of Glass", in which he showed that since 1921, when the theory was propounded by Prof. A. A. Lebedev, many facts had been established that confirmed the presence in glass of ordered regions (crystallites), a phenomenon that is compatible with the phase diagrams of the systems studied. At the same time, during the intervening years, the crystallite theory has been developed and improved as our knowledge of the various properties of glass has extended. The present views on the structure of glass are formed by an integration of the theories of amorphous or network structure with the principles relating to crystallite formations. The modern crystallite hypothesis regards glass as a complex system, in which both crystalline and amorphous elements exist side by side, and it is of great importance to determine the relative volumes occupied in this structure by the ordered and amorphous parts.

In a paper by Corr. Memb. Acad. Sci. USSR P. P. Kobeko, entitled "Structure and Properties of Organic Glasses", it was shown that, on the basis of the classical studies of A. A. Lebedev and A. L. Strozharov, it must be considered that equilibrium amorphous structures must exist in a substance at below its melting point.

In his paper on the "Structure of Glass", Prof. O. K. Botvinkin suggested that the main structural elements characteristic of glasses were molecular groupings formed during the gradual cooling of the melt.

V. P. Barzakovsky Doc. Chem. Sci., who discussed D. I. Mendeleev's paper, "Composition of Silica Compounds" as giving the first scientific theory of the structure of silicates, cited much recently discovered archive material, which showed that already in 1856 D. I. Mendeleev had built up an original chemical theory of the structure of silicates, differing essentially from the views of his predecessors and deeply penetrating into the essential nature of compounds of silicic acid. At the same time, Mendeleev suggested polymeric structures for silica and silicates.

Prof. V. V. Tarasov, in his paper on the "Quantum Theory of Specific Heats and the Structure of Silicate Glasses", gave an account of the results of his investigations on the quantum theory of the specific heats of chain and layer structures. The method developed by the author enabled determinations to be made of the vibration of the silicon-oxygen skeleton taken as a whole, and enabled conclusions to be reached concerning the architecture of the skeleton.

In her paper on "Concepts of the Internal Structure of Glasses Arising from the Results of an Investigation of Certain Properties of the Glasses of Simple Systems", L. I. Demkina Doc. Tech. Sci. showed that, when hyperbolic curves are transformed into straight lines on "composition-property" diagrams, and particularly on the "property-property" diagrams presented by the lecturer, discrete changes in properties may be detected, and these occur at compositions lying between definite chemical compounds and near to the eutectic points.

In a paper by Professors O. A. Esin and P. V. Geld, many facts were presented that indicated the energetic nonequivalence of ions in silicate melts and the microheterogeneity associated with this. These systems, in the authors' opinion, consist entirely of ions of various degrees of complexity. It may be supposed that glasses also consist of heteropolar formations, i.e. their structural elements are ions.

A. A. Appen Cand. Chem. Sci., in his paper on the "Coordination Principle of Arrangement of Ions in Silicate Glasses", showed that the properties of glass were determined not only by its composition, but also by its structure. The main structural factors that greatly affect the properties of glass are the degree of binding in the silicon-oxygen skeleton and the coordination state of the cations.

In his paper on the "Structure of Glass According to the Results of Investigations on the Structure of Porous Glasses and Films", **S. P. Zhdanov** Cand. Chem. Sci. discussed the results of investigations on porous glasses obtained by the leaching of sodium borosilicate glasses. The mechanism by which the formation of porous glasses is found to occur indicates that the original glass is on the whole heterogeneous in composition. The dimensions of these heterogeneous regions vary from tens to hundreds of Angstroms.

In their paper on "Raman Scattering and the Structure of Vitreous Substances", **Corr. Memb. Acad. Sci. USSR E. F. Gross** and **V. A. Kolesova** stated that the spectrum of inorganic glasses having low softening points (the system $\text{KNO}_3-\text{NaNO}_3-\text{Ca}(\text{NO}_3)_2$ and pyrophosphoric acid) does not change essentially when the substance passes from the liquid to the vitreous state, which is an indication of the similarity in structure of the substance in these two states.

In a study of two-component silicate glasses of the systems $\text{Na}_2\text{O}-\text{SiO}_2$ and $\text{K}_2\text{O}-\text{SiO}_2$, it was shown that the spectrum of the glass changes in regular fashion as the alkali content of the glass is increased. Hence, spectroscopic methods for the investigation of glasses have as yet given no proofs of the existence of crystallites in glass.

V. A. Florinskaya Cand. Phys. Math. Sci. and **R. S. Pechenkina** in a paper on the "Spectra of Simple Glasses in the Infrared Region, and Their Relation to the Structure of Glass" communicated the results of a comparison of the infrared spectra of original and devitrified glasses; broadening of the bands in the spectra on passing from devitrified to homogeneous glass indicates, in the authors' opinion, that in the latter there exist groups of atoms having an ordered array, similar to the array found in the lattice of the corresponding silicate.

In his paper on the "Possibilities and Results of X-Ray Methods of Investigating Vitreous Substances", **E.A. Porai-Koshits** Cand. Phys. Math. Sci. showed that the X-ray analysis of simple (one-component) glasses proved beyond doubt that large regions of inhomogeneity having dimensions of greater than 15-20 Å were absent. **E.A. Porai-Koshits** discussed also the results of a study of the products of leaching sodium borosilicate glasses by the method of X-ray scattering at very low angles. These results enabled the regions of heterogeneity in the original glasses to be determined.

A. I. Stozharov Cand. Phys. Math. Sci., in his paper on the "Thermal Expansion of Glasses in its Relation to the Question of the Structure of Glass", gave the results of a careful study of the thermal expansion curves of glasses, on which breaks could be detected that could be ascribed to definite components of the glasses.

Active Memb. Acad. Sci. Byelo Russian SSR A.N. Sevchenko, in his paper on the "Use of the Luminescence Method for the Study of the Vitreous State", showed, on the basis of experiments on uranyl glasses, that this method permits the investigation of the immediate surroundings of the centers of luminescence, i.e. the super-fine structure. The experimental results of an investigation of quenching and of luminescence spectra at various stages of quenching for uranyl glasses show that the vitreous state should be regarded as a dispersion of finely crystalline formations (crystallites) in an amorphous pseudo-solution of glass.

V. A. Ioffe Cand. Phys. Math. Sci. gave an account of the results of his investigations on the dielectric losses in simple glasses (alkali and lead binary systems) at low temperatures and at high and super-high frequencies.

In his paper on the "Rayleigh Scattering of Optical Glasses, and the Structure of Glass", **D.I. Levin**, Cand. Phys. Math. Sci., showed that molecular (Rayleigh) scattering is the result of heterogeneity in the actual structure of the optical and sodium borosilicate glasses investigated, and is not due to "frozen-in" deformation and strains.

S.K. Dubrovo Cand. Chem. Sci., in his paper on the "Instability of Vitreous Silicates and Aluminosilicates toward Aqueous Solutions, and its Relation to the State of Silica in Glass", associated the chemical stability of glass with its crystallochemical characteristics, showing that the passage of Na_2O , Al_2O_3 , and SiO_2 into solution in presence of acids is determined by the nature of the bonds in the aluminum-silicon-oxygen skeleton of the glass.

In her paper on the "Chemical Stability of Glasses of the Ternary System Sodium Oxide--Boric Anhydride Silica", O.S. Molchanova showed that the reactivity of these glasses toward aqueous solutions depends on the state of boron in the glass and the possibility of the formation of water-soluble compounds as a result of the reactions.

The formation of porous glass is a result of the hydration of silica, not only at the point of rupture of the O-Na bond, but also of the bonds of B-O-Si.

Papers by Yu. A. Gastev and A.F. Zak considered questions relating to the chemical stability of glass. New data concerning the properties of complex glasses were communicated by Prof. M.M. Gurevich, A.G. Repa, G. A. Stepanov, and L.A. Afanasyev. A detailed exposition of the works of D.I. Mendeleev was given by L.G. Melnichenko in his paper on the "Theoretical Views of D.I. Mendeleev on the Structure of Silicates and Glass, and Their Significance for Modern Science".

In the discussions that followed descriptions were given of new experimental investigations, and the fundamental problems of the structure of glass, already portrayed by the lecturers, were discussed in particular detail.

Prof. A. I. Avgustiniuk referred to investigations on the micro-hardness and reflection spectra of glasses obtained by the fusion of feldspar with various additions. It was found that the micro-hardness of a fine-polished surface of glass was considerably different (generally higher) than that of glass after grinding and polishing with rouge, which is explained by the author by the formation of crystallites of stable chemical composition suitably oriented at the surface. The reflection spectrum of glasses of enhanced micro-hardness contains a line corresponding to the linkage Si-O-Al. D. I. Dobychin, Cand. Chem. Sci., considered, on the basis of his investigations, that, when opalescent glasses of the $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$ system are leached with acid, no secondary silicic acid is formed in the pores.

N. K. Voskresenskaya, Doc. Chem. Sci., has shown that many of the salt combinations that she has studied form melts in which a "tendency to form layers" is observed, which indicates the existence of micro-regions in the melts that differ among themselves greatly in composition. A similar micro-heterogeneity must remain in supercooled melts, and therefore also in glasses.

Prof. G.M. Bartenov demonstrated the incorrectness of both of the extreme points of view on the structure of glass: as a polycrystalline formation, and as a completely disordered network. The ordered regions, 15-20 Å in size, assumed to exist in simple glasses cannot serve as nuclei for a new phase and are regions of close order without defined limits.

Academician N.V. Belov pointed out that the structural unit of a silicate glass, as established by X-ray analysis, is the SiO_4 tetrahedron, but the methods of X-ray analysis are not able to give a more detailed picture of the arrangement of atoms in glass. In order to speak of crystallites, these must contain about 10,000 elementary cells; only then can the X-ray methods give any indications concerning their structure.

N.V. Belov considered that the basic idea of Zachariasen concerning the presence of a disordered silicon-oxygen network in glass is correct. It is, however, necessary, as A.A. Appen has done, to take into account the possibility of differentiation, resulting in the formation of regions corresponding in composition to definite chemical compounds. In the solidification of melts, there is a continuous piling up of SiO_4 tetrahedrons, forming defined "fragments" of anionic radicals.

In N.V. Belov's opinion, there is no need to assume that spaces (vacuoles) filled with borates exist in borosilicate glass. In the cooling of a borosilicate glass, a considerable proportion of the BO_4 tetrahedra are converted into triangles. As a result, weak places are formed that are susceptible to the action of water or acids.

Modern crystal chemistry, stated Prof. G.B. Boky, has established that molecules do not exist in silicates, so that to assume the existence of molecular groupings in glass, as Prof. O.K. Botvinkin does, is incorrect. In glass there are ordered regions. It does not follow from this, however, that we must reject Zachariasen's hypothesis and confine our attentions to the crystallite theory of the structure of glass. There are no unreconcilable contradictions between the crystallite and continuous-network theories. In glass there are ordered and less ordered regions between which there are continuous transitions, and there are no phase boundaries. This viewpoint, which is a synthesis of the two theories, must be placed at the basis of concepts concerning the structure of glass.

Prof. V. Ya. Anosov pointed out that geometric transformations of diagrams, such as those made by L.L. Demkina, must always be subjected to mathematical analysis, since otherwise particular characteristics may disappear from or appear in the curves and lead to incorrect interpretation. Prof. Anosov considered that it is impossible to speak of a discrete point on curves expressing the properties of glass; it is better to use the term "break" or "singular point". Prof. Anosov also warned against the incorrect concept of a liquid as a chaotic

assembly of molecules.

V.S. Molchanov considered that those defending the primitive crystallite theory are insufficiently acquainted with the history of the question. In fact, the author of the crystallite theory, Academician A.A. Lebedev, stated in 1940 that between the continuous-network and crystallite theories "there is strictly speaking no essential difference; there is only a quantitative difference". The history of the conflict between the crystallite and Zachariasen hypotheses and of their development is similar to that of the conflict between the corpuscular and wave theories of light; it is an example of the conflict of contradictions and of the higher synthesis of these contradictions.

Prof. G.I. Skanavi considered that the vehement discussion at the conference did not derive from the apparently opposed positions ("crystallite" and "network") taken by the disputants, but was concerned rather with the fact that some were talking about the macroscopic properties of the system (viscosity, crystallization, thermodynamic stability), and others were trying to propose methods that would reveal the microstructure of glass although there are still no unequivocal experimental methods for the determination of structure of the close-order regions in glass. In G.I. Skanavi's opinion, the most hopeful direction of work in this field is the study of dielectric losses, which are most closely associated with the details of the structure of glass.

Active Memb. Acad. Sci. Byelo Russian SSR M.A. Bezborodov, referring to the great significance of the work of Academician A.A. Lebedev, pointed out that the crystallite hypothesis of A.A. Lebedev had infused new blood into the science of the vitreous state of matter. It constituted daring scientific innovation, and it demanded a fundamental review of obsolete concepts concerning the structure of glass. It determined also the further course of investigations on vitreous substances both here and abroad.

Prof. N.A. Toropov considered that the main problem confronting the investigators of glass was the determination of the relative dispositions and coordinates of the separate material particles. This difficult problem is not a hopeless one, and a time will come when we shall have as clear a concept of the structure of glass as we have of the structure of crystals. The investigation of the extremely fine mechanism of the formation of a larger ordered region - a crystalline nucleus in glass - forms one of the ways of solving the problem of the vitreous state. Great significance for the understanding of the vitreous state is associated with the study of the solid solutions and crystalline phases of variable composition that are often observed in complex silicate systems.

Workers on the structure of silicate glasses must keep in close touch with the investigators of organic glasses. From what may sometimes appear to be conflicting concepts, a more correct picture, reflecting the full complexity of the substances studied, may develop.

Other participants in the discussion were Prof. N.V. Solomin, Prof. K.G. Kumanin, Prof. I.F. Ponomarev, Prof. A.G. Bergman, and Candidates of Science V.A. Presnov, G.O. Bardykyants, V.T. Slavyansky, L.V. Sergeev, Yu. N. Andreev, B.I. Markin, V.P. Pryanishnikov, and others.

Summing up the conference, Academician A.A. Lebedev stated that as a result of the lively discussion the question of the structure of glass had been considerably clarified, and common points of view had been established. Everyone now agreed that there are ordered and disordered regions in glass, and whether we should call them crystallites or regions of close order or a network having an ordered arrangement of lattice points - this is a terminological question. We may consider that at the present time our picture of the structure of glass is fairly clear from the qualitative point of view. It is now necessary to pass to the next stage of the study of vitreous substances - to the quantitative side of the question. For example, we do not yet know the dimensions of the ordered and disordered regions in glass.

We can arrive at an understanding of the structure of glass only as a result of the application of numerous fine methods of investigation, and only when the results of many methods agree can we make reliable inferences.

In the resolution that was passed concerning the "Present State and Ways of Further Development of the Theory of the Structure of Glass", it is stated "that the development of the crystallite hypothesis and the hypothesis of close order has now resulted in a unified point of view on the question of spatial order in the arrangement of atoms in glasses (which indicates the presence of chemical bonds)".

"The Conference considers that one of the main problems is the creation of a general theory of the structure of vitreous substances, which would explain, not only qualitatively, but also quantitatively, the main characteristic features of structure present in glasses of all types, i.e. vitreous forms of elements and one-component and complex inorganic and organic glasses.

"The Conference considers that it is of extreme importance to seek and develop a method that would permit the establishment of the spatial disposition of the atoms, ions, and molecules in glasses with the same degree of probability as this can be done by X-ray analysis for crystalline substances."

A large section of the resolution was devoted to the enumeration of concrete problems confronting the research organizations working on vitreous substances. Thus it is proposed to intensify or renew work on X-ray, electron, and neutron diffraction investigations of the structure of glasses, on electron microscope and ultrasonic investigations, on infrared, ultraviolet, and Raman spectra, on luminescence and Rayleigh scattering, on the variation over a wide temperature range of optical, electrical, mechanical, and other properties of glasses, on the application of the method of labeled atoms, of the quantum theory of specific heats, of methods of physicochemical analysis, and so on.

It was considered that another important problem is the establishment of an agreed terminology for the description of the structure of glasses, and the Institute of Silicate Chemistry of the USSR Academy of Sciences was allotted the task of developing a new terminology project.

The Conference considered that it was very unsatisfactory that many authors should treat their experimental results in an excessively biased way - from the point of view of a single one of the existing hypotheses on structure - and it expressed the hope that, in newly published literature (including textbooks), an objective and critical treatment would be given of the present state of the theory of the structure of glasses and of the historical development of the various hypotheses.

The resolution concluded by pointing out the need to intensify work on the philosophical generalization of the concrete experimental material relating to questions concerning the structure of glass, and the need also to develop the historical side of the chemistry and technology of glass in our country, emphasizing particularly the significance of the works of Lomonosov and Mendeleev.

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